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GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF RESEARCH ADMINISTRATION

RESEARCH PROJECT INITIATION

(Revised-Correction of Project Period)

Date: August 2, 1974

Project Title: Development of Ultraviolet Protection Nomex Data

Project No: E-27-623

Principal Investigator: Dr. W. C. Tincher

Sponsor: U. S. Air Force, AFSC Aeronautical Systems Division, Wright-Patterson AFB, Ohio

Agreement Period: From May 28, 1974 Until ~~September 25, 1975~~* (R&D Performance Period)

Type Agreement: *15 months from contract mailing date.
Contract No. F33657-74-C-0716

Amount: $63,264

Reports Required: Monthly R&D Status, Final Technical, Process Specification

Sponsor Contact Person (s):

Technical Matters	Administrative Matters (thru ORA)
LIFE SUPPORT SPO	Mr. R. J. Whitcomb, (ACO)
ATTN: ASD/SML-3	ONRRR
AFSC Aeronautical Systems Div.	
Wright-Patterson Air Force Base, OH 45433	

Assigned to: ~~School of Textile Engineering~~

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RA-3 (6-71)

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SPONSORED PROJECT TERMINATION

Date: April 28, 1977 adb

Project Title: *Development of Ultraviolet Protection Nomex Data*

Project No: *E-27-623*

Project Director: *Dr. Wayne C. Tincher*

Sponsor: *U. S. Air Force, AFSC Aeronautical Systems Division*

Effective Termination Date: *2/29/76*

Clearance of Accounting Charges: *2/29/76*

Grant/Contract Closeout Actions Remaining:

- _ Final Invoice and Closing Documents
- _ Final Fiscal Report
- X Final Report of Inventions
- _ Govt. Property Inventory & Related Certificate — Submitted 10 Feb 77
- _ Classified Material Certificate
- _ Other _____

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CA—4 (3/76)

E-27-623

Monthly Progress Report Number 1

(June 26, 1974 - July 26, 1974)

Development of Ultraviolet Protection Nomex

Life Support SPO
Air Force Systems Command
Aeronautical Systems Division
Wright-Patterson Air Force Base, Ohio 45433

(Prepared Under Contract No. F33657-74-C-0716
by
Georgia Institute of Technology
Atlanta, Georgia 30332
W.C. Tincher, author)

Summary

A computer literature search is underway to assemble published data on UV stabilizers for Nomex and other aromatic polyamides. References to the mechanism of UV degradation of Nomex and to methods for incorporating stabilizers in the fiber are also being collected. Three recommended stabilizer components have been found to date and two of these will be investigated in the initial screening studies. Several important papers have been published on the mechanism of UV degradation of Nomex. These papers indicate that radical scavengers and antioxidants may be effective in stabilization of Nomex.

The first scheduled meeting with Air Force personnel at Wright-Patterson Air Force Base was held on July 25, 1974. A review of the importance of the Nomex UV degradation problem and a summary of sponsored research in this area were presented by Air Force personnel. An outline of the current research and development effort was presented and discussed and decisions were reached on a number of technical and administrative details.

TABLE OF CONTENTS

I. Introduction

The purpose of this project is to develop stabilizer systems for reducing the loss of desirable physical properties of Nomex fabrics and webbing on exposure to UV radiation. Nomex loses up to 80% of its breaking strength after exposure for 100 hours in a carbon are Fade-Ometer. This sensitivity to UV exposure severely limits the utilization of Nomex for many applications in which its thermal stability and flame resistance could yield significant advantages.

The proposed research and development program will be conducted in three phases. First, a survey of the published literature will be conducted for information on compounds which are reported to improve the UV stability of Nomex. Compounds selected on the basis of this survey, materials recommended by stabilizer manufacturers,and components expected to interrupt the Nomex degradation mechanism will be applied to Nomex yarn and tested for effectiveness in reducing UV degradation. Second, a series of one or more designed experiments are planned to determine required concentration of stabilizer components and the most effective combinations of components for development of stabilizer systems. Third, a system will be selected and tested on parachute fabric and webbing to evaluate the degree of protection against UV degradation which can be achieved. The target is 75% strength retention of Nomex cloth after 150 hours exposure in a Weather-O-Meter.

II. Literature Survey

A previous literature survey has been published (1) on UV degradation and stabilization of Nomex covering the literature prior to

1970. The current search has concentrated, therefore, on literature published since that time.

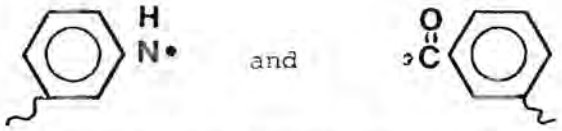
The major effort in the literature survey has been a computer search of Chemical Abstracts. The descriptor index used in this search is shown in Table 1. The program is designed to select articles which have the following combinations of descriptors:

G001
G002 + G003 + G004 + G005
G003 + G004 + G005 + G006 + G007
G005 + G006 + G007 + G008
G009 + G003 + G004
G008 + G005

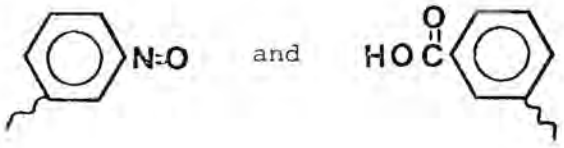
The computer search will be supplemented by information from fiber and stabilizer manufacturers and by searches of other abstracting services.

The literature search at the present time has yielded three compounds that are reported to improve the UV stability of Nomex or other aromatic polyamides. These compounds are sulfur dyes (2), Tinuvin P (1), and carbon black (1). The first two of these (or suitable variations) will be utilized in the stabilizer component screening studies.

The literature search has uncovered a number of important articles on the mechanism of degradation of Nomex (3-5). This work suggests that Nomex degrades by chain cleavage at the amide bond giving the two radicals



These undergo reaction with oxygen to yield



The nitroso group (-N=O) probably undergoes further reaction. These results suggest that radical scavengers and antioxidants may have some beneficial effects in reducing the UV digradation of Nomex.

The UV radiation responsible for Nomex degradation has been studied by a number of workers (4,6). Nomex absorbs UV radiation beginning at approximately 390 nanometers (mm) and extending into the near UV with a peak at approximately 360 nm. This absorption is responsible for both the yellowing of the fiber and the loss in tensile strength (6). It is unlikely that conventional screening agents with absorption peaks further in the UV will be useful in stabilizing Nomex. Fluorescent brightening agents should, however, be effective in competing with the Nomex substrate for radiation near 360 nm. Several fluorscent brightners substansive to amides will be among the initial compounds selected for screening.

Thus, although large numbers of specific compounds for UV stabilization of Nomex have not been reported in the literature, the available information on degradation mechanisms should provide a basis for judicious selection of stabilizer components for the screening experiments.

III. Technical Review of Proposed Research

As specified in the contract, the first meeting at Wright-Patterson Air Force Base to discuss the research effort was held on July 25, 1974. The problems encountered due to poor UV stability of Nomex were described and the limitations that this property deficiency places on use of Nomex in Air Force systems was ex-

plained by Air Force personnel. In addition, a brief review of previous Air Force sponsored research and in-house efforts on UV stability of Nomex was presented.

The proposed research effort, under the current contract, was outlined and a proposed "milestone" chart discussed. The "milestone" chart was acceptable with some minor modification and is shown in Table 2.

Several technical details were also discussed. It was mutually agreed that initial screening studies for stabilizer component would be conducted on Sage Green Nomex Yarn with promising candidates further evaluated on natural yarn samples. It was also decided that the designed experiment for selection of stabilizer systems may be replicated one or more times if several promising components of a given type are found to be effective in stabilization of Nomex.

Administrative details were also discussed. It was suggested that monthly reports should be received at the sponsor's office by the 30th of each month with the first report scheduled for July 30, 1974.

The trip concluded with a tour of the fiber and fabric testing facilities of the Air Force Materials Laboratory with special attention to the fammability test facilities and procedures that will be necessary for testing thermal stability of Nomex samples containing UV stabilizers.

IV. Future Work

Durning the next month the first series of stabilizer components

for screening tests will be selected and all materials and supplies assembled to begin the screening program.

V. References

1. Krasny, J.F. and Swartz, A.M., Nomex Ultraviolet Inhibitors, ASD-TB-72-104, August, 1972

2. Author's unpublished data.

3. Carlsson, D.J. and Wiles, D.M., "High Performance Fibers, Part I: Types, Properties, and Applications", Canadian Textile Journal, 90, 6: 107 (1973).

4. Blais, P., Carlssm, D.J. Parnell, R.D., and Wiles, D.M., "High Performance Fibers, Part II: Limitations, Photo and Thermal Degradation, Canadian Textile Journal, 90, 7:93 (1973).

5. Carlssm, D.J., Parnell, R.D. and Wiles,D.M., "The Photo-degradation of Poly (1,3, Phenylene Isophthalamide Films Under Vacuum.", Polymer Letters, 11, 149 (1973).

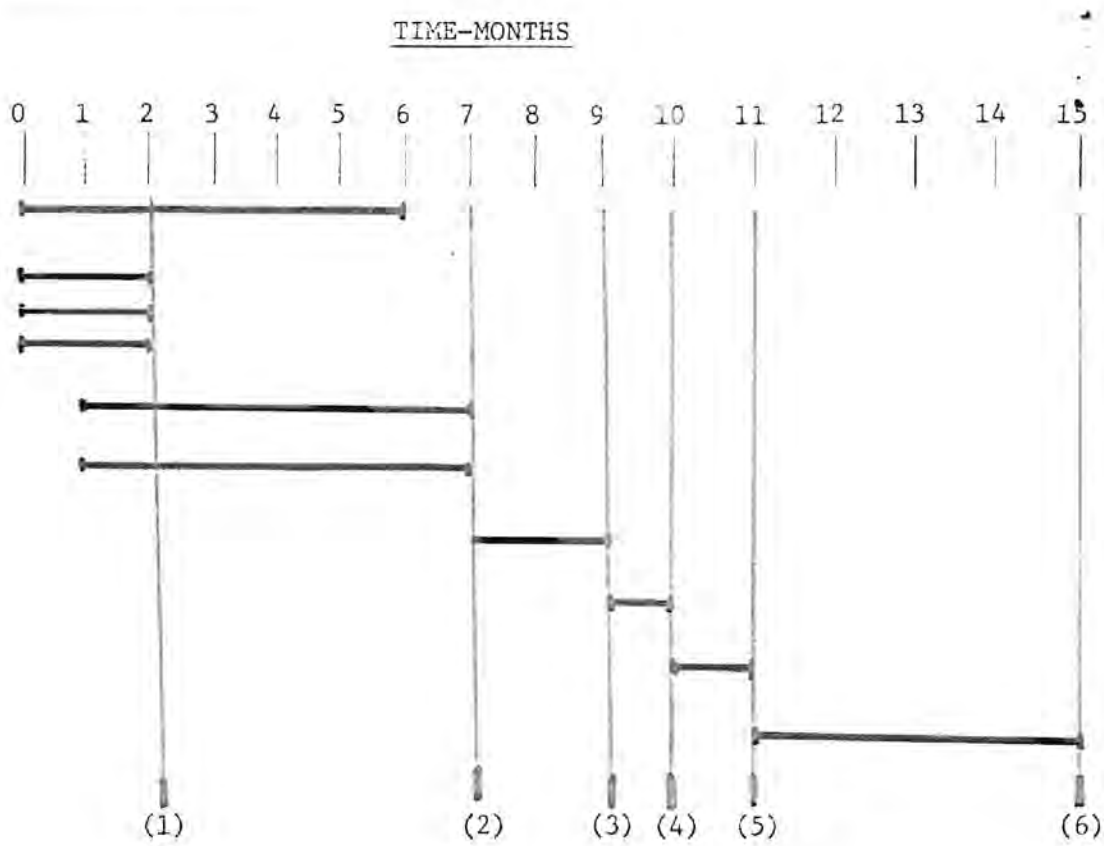
6. Johnson, L.D., Tincher, W.C., and Bach, H.C. "Phototegradtion Wavelength Dependence of Thermally Resistant Organic Polymers", Journal of Applied Polymer Science, 13, 1825 (1969).

TABLE I

Descriptors in Computer Literature Search

Group	Term No.	Term	Group	Term No.	Term
G001	1	NOMEX	G005	31	DEGRAD*
G002	2	AROMATIC*	G005	32	DEGRDN
G002	3	AROM	G005	33	BREAKDOWN*
G002	4	*BENZ*	G005	34	BREAK-DOWN*
G002	5	*ISOQUINO*	G005	35	BREAKING DOWN*
G002	6	*INDOL*	G005	36	UNZIP*
G002	7	*INDEN*	G005	37	CLEAV*
G002	8	*INDAZOL*	G005	38	*STABIL*
G002	9	*INDANYL	G005	39	*STABLE
G002	10	*FLUOREN*	G005	40	DETERIORAT*
G002	11	*PHENYL*	G005	41	DEGENERAT*
G002	12	*PHTHAL*	G005	42	REACTION*
G002	13	*TOLYL*	G005	43	DEPOLYMERIZ*
G002	14	*PYRIDYL*	G005	44	DEPOLYMN
G002	15	*NAPTHYL*	G005	45	HYDROLY*
G002	16	*ARYL*	G005	46	SOLVOLY*
G002	17	*ANTHRYL*	G005	47	PHOTOLY*
G002	18	ARENE	G005	48	REACTION*
G003	19	POLY*	G006	49	HEAT
G003	20	MACROMOL*	G006	50	THERMAL*
G003	21	MACRO-MOL*	G006	51	*FLAM*
G004	22	*AMIDE*	G006	52	FIRE*
G005	23	UV	G007	53	RESIST*
G005	24	U.V.	G007	54	*PROOF*
G005	25	U. V.	G007	55	*RETARD*
G005	26	ULTRAVIOLET	G008	56	NYLON
G005	27	ULTRA-VIOLET	G009	57	HIGH TEMP*
G005	28	LIGHT	G009	58	NONFLAMMABLE
G005	29	DECOMPCS*	G009	59	NON-FLAMMABLE
G005	30	DECOMPN			

Table 2
MILESTONE CHART



(1) AT LEAST 10 CANDIDATE STABILIZERS SELECTED FOR SCREENING
(2) SELECTION OF AT LEAST 3 STABILIZERS FOR DESIGNED EXPERIMENT
(3) SELECTION OF 4 STABILIZER SYSTEMS FOR FABRIC TESTING
(4) SHIPMENT OF 4 FABRIC SAMPLES FOR AIR FORCE TESTING
(5) SELECTION OF BEST SYSTEM FOR FABRIC AND WEBBING SAMPLES
(6) SHIPMENT OF FABRIC AND WEBBING SAMPLES

E-27-623

Monthly Progress Report Number 2

(July 26, 1974 - Aug. 26, 1974)

Development of Ultraviolet Protection Nomex

Life Support SPO
Air Force Systems Command
Aeronautical Systems Division
Wright-Patterson Air Force Base, Ohio 45433

(Prepared Under Contract No. F33657-74-C-0716
by
Georgia Institute of Technolgoy
Atlanta, Georgia 30332
W. C. Tincher, author)

Summary

The computer literature search has been broadened to include U.S. Government Research and Development Reports in addition to Chemical Abstracts. A manual search of Textile Technology Digest has also been conducted. One patent has been uncovered with recommended compounds for improvement of Nomex dye lightfastness.

Discussions with manufacturers of Nomex and with 5 companies manufacturing light stabilizers have been held. As a result of these discussions a total of 12 compounds have been selected for initial stabilizer component screening. Ultraviolet absorbers, antioxidants, and radical scavengers are all included in the materials to be screened.

TABLE OF CONTENTS

I. Introduction

During this month major effort has been directed toward contacts with manufacturers of UV screening agents, antioxidants, radical scavengers, fluorescent brighteners and other materials which may be of interest in improving the UV stability of Nomex. The literature survey has continued with several other sources searched and some descriptors added to the list.

II. Literature Survey

In addition to Chemical Abstracts the computer literature search has been extended to the U.S. Government Research and Development Report tapes. These tapes cover the period 1970 to the present. The computer searches have been supplemented by manual search of Textile Technology Digest for the period 1969 to the present.

Based on experience with the computer search, the list of descriptors has been expanded by addition of the terms shown in Table 1. This expanded list should provide greater assurance that pertinent references will not be missed.

TABLE 1

Additions to Descriptor List

Aramid
Poly (1,3-Phenylene Isophthalamide)
Poly (1,4-Phenylene Terephthalamide)
Poly (1,3-Phenylene Terephthalamide)
Poly (1,4-Phenylene Isophthalamide)
Poly (4-aminobenzoic acid)
Poly (3-aminobenzoic acid)
Kevlar
Fiber B
HT-1
HT-4
PRD49
Kynol
Polybenzimidazole
Poly(benzimidazole)
PBI

Two new significant references have been uncovered this month. One, a patent (see Reference 1), describes the addition of UV screening agents to Nomex for improvement in dye lightfastness. Two screening agents, Uvinul D-49 and Tinuvin 327, were used in this study.

The second reference[2], although unrelated to Nomex, may provide some insight into the degradation mechanism. It is reported that dyes containing aromatic amide groups exert a significant phototendering effect when applied to cellulose fiber. Preferential reaction of the photo-excited state of aromatic amides with hydroxy or ether groups may provide a means for deactivating the excited species.

With the exception of these references and those mentioned last month the literature survey has provided little guidance for selection of stabilizers for Nomex.

III. Survey of Manufacturers

A number of contacts have been made within the Dupont Company and with manufacturers of chemical additives for stabilization of polymers against UV degradation. These contacts are summarized below.

A. E. I. duPont de Nemours & Company

Discussions of the Nomex UV stability problem were held with Dr. Calvin J. Cruz, Supervisor Nomex Technical Service and Dr. Bob Thomas, Jackson Laboratory. Dupont's major interest has been in the dye lightfastness of Nomex because this property has limited application of Nomex in commercial aircraft interiors. A new fiber modification with improved dye lightfastness is being introduced by Dupont in the next few months. No information was

available on how this modification would affect strength retention properties of the fiber on UV exposure.

At the present time Dupont is adding a UV screening agent to both colorsealed sage green (Type 433) and olive green (Type 432) Nomex. There is little evidence that the additive is effective but they have been reluctant to change the production process by removing it.

The Jackson Laboratory has conducted fundamental studies on the mechanism of degradation of dyes on Nomex. They have agreed to discuss the results of these studies with us. The Dupont physicist conducting the study will contact me.

B. Ciba-Geigy

Ciba-Geigy appears to be the only manufacturer of stabilizers that is aware of the Nomex light stability problem and that has conducted some work in the area. Several Ciba-Geigy materials in the Tinuvin series of UV screening agents and the Irganox series of antioxidants will be screened for stabilization of Nomex. We also requested samples of an experimental material GI-10-460 (an aromatic diamide of oxalic acid) which is reported to be a light stabilizer (3).

The possible use of optical brighteners as screening agents for Nomex was discussed with personnel at the Greensboro Laboratory of Ciba-Geigy. The major difficulty with optical brighteners is that they show poor fastness to light and might therefore degrade too rapidly to be effective in screening Nomex. Optical brighteners samples with the following characteristics

1. Substansive to amides
2. Good lightfastness
3. Strong absorbers in 320-400 nm region

were requested for screening studies.

TABLE 2

Compounds For Initial Screening Experiments

UV ABSORBERS

Uvitex RBNAD
Uvitex NFW
Uvitex 4BMA
Tinuvin 328
GI-10-460

ANTIOXIDANTS

Irganox 1098
Irganox 1010
Irganox 1035

FREE RADICAL SCAVENGERS

Irgastab 2002
Ferro AM-105
Collodial Sulfur
Maganese Hypophosphite

C. Other Manufacturers of Stabilizers Candidates

In addition to Dupont and Ciba-Geigy, conversations have been held with representatives of American Cyanamide, Sandoz, Eastman Chemical Products, and Ferro Corporation. The Nomex stability problem was discussed and each company agreed to send samples of materials they manufacture or have under development which might provide UV protection for Nomex. Stabilizer candidates for screening will be selected from these materials based on their structure and likely mode of action in interrupting the

Nomex degradation mechanism. Contacts with several other stabilizer manufacturers are planned in the coming month.

IV. Stabilizers Selected for Screening.

The compounds shown in Table 2 have been selected for the initial screening for stabilizer components. Three types of stabilizers are represented - UV absorbers, antioxidants, and radical scavengers/excited state reactants.

1. UV Absorbers

The absorption spectrum of Nomex in the near UV is shown in Figure 1 (4). To be an effective screening agent the UV absorber must compete effectively with Nomex for photons in this region. The UV absorbers in Table 2 have been selected for strong absorption in this region. A typical absorption curve for Uvitex RBNAD is shown in Figure 2. Similar curves have been obtained for other UV absorbers.

2. Antioxidants

The hindered phenols have been one of the most effective groups of compounds that act as antioxidants. The Irganox compounds are hindered phenols with amide, ester, and thioglyoxal substituent groups.

3. Radical Scavengers/Excited State Reactants

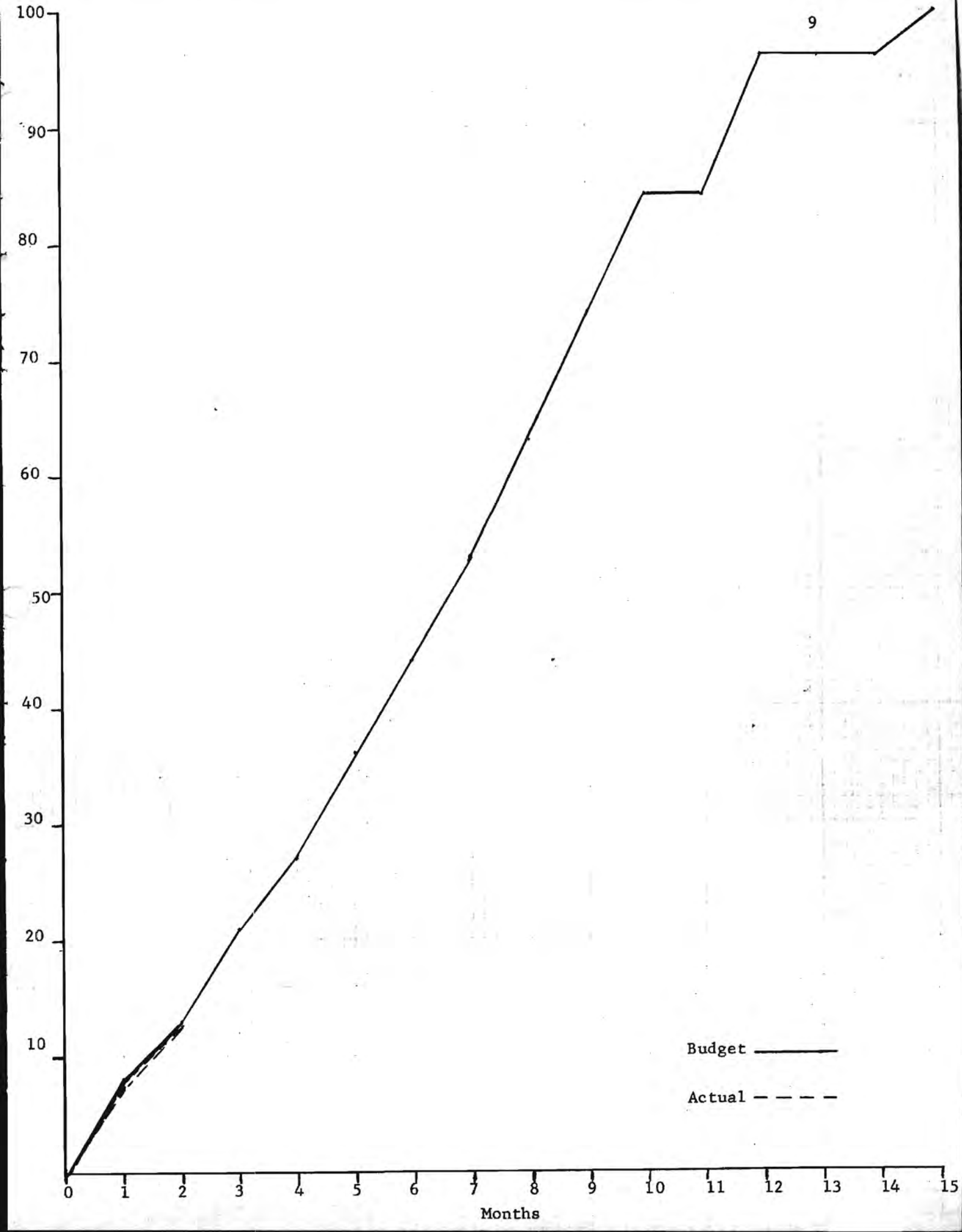
Sulfur, organometallic compounds, and metallic salts have been effective in stabilizing aliphatic amides probably by reaction with either free radicals or with excited species produced by the absorption of light. The compounds of this type shown in Table 2 have been effective in stabilizing other polymers against UV degradation. Their effectiveness in Nomex will be determined.

V. Future Work

Initial screening experiments will begin next month. Samples of stabilizers are on hand and exposure and testing equipment has been prepared and checked. Studies can begin immediately on receipt of the Nomex yarn from Dupont.

VI. Budget

The funds budgeted and either expended or encumbered for the first two months are shown on the attached graph.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Months
Budget
Actual

VI. References

1. Hermes, Julius, "Pretreatment and Dyeing of Shaped Articles Derived From Wholly Aromatic Polyamides", U.S. Patent 3,771,949, Nov. 13, 1974.

2. Venkataraman, K., "The Chemistry of Synthetic Dyes", Volume II. Academic Press Inc., 1952, pp. 1228-1244.

3. Luethi, C. et al, "Bis (Oxalic Acid Aromatic Diamide) Ultraviolet Polymer Stabilizers", South African Patent 68-19932, August 28, 1968.

4. Textile Fiber Department, E. I. duPont de Nemours & Co., "Determining the Lightfastness of Cationic Dyes on Nomex Nylon", Preliminary Information Memo Number 216, Jan. 5, 1971.

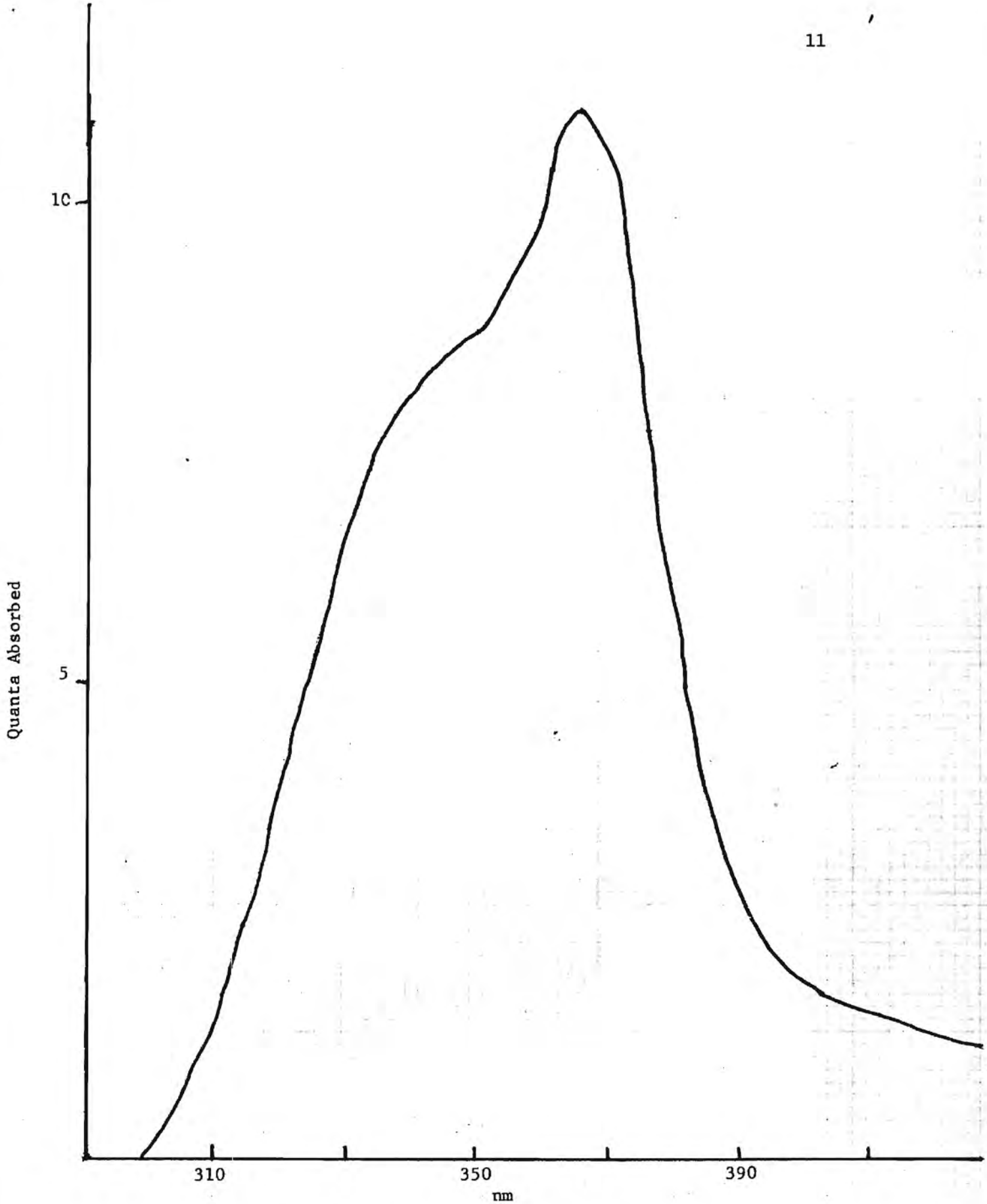


Figure 1 - Absorption Spectrum of Nomex

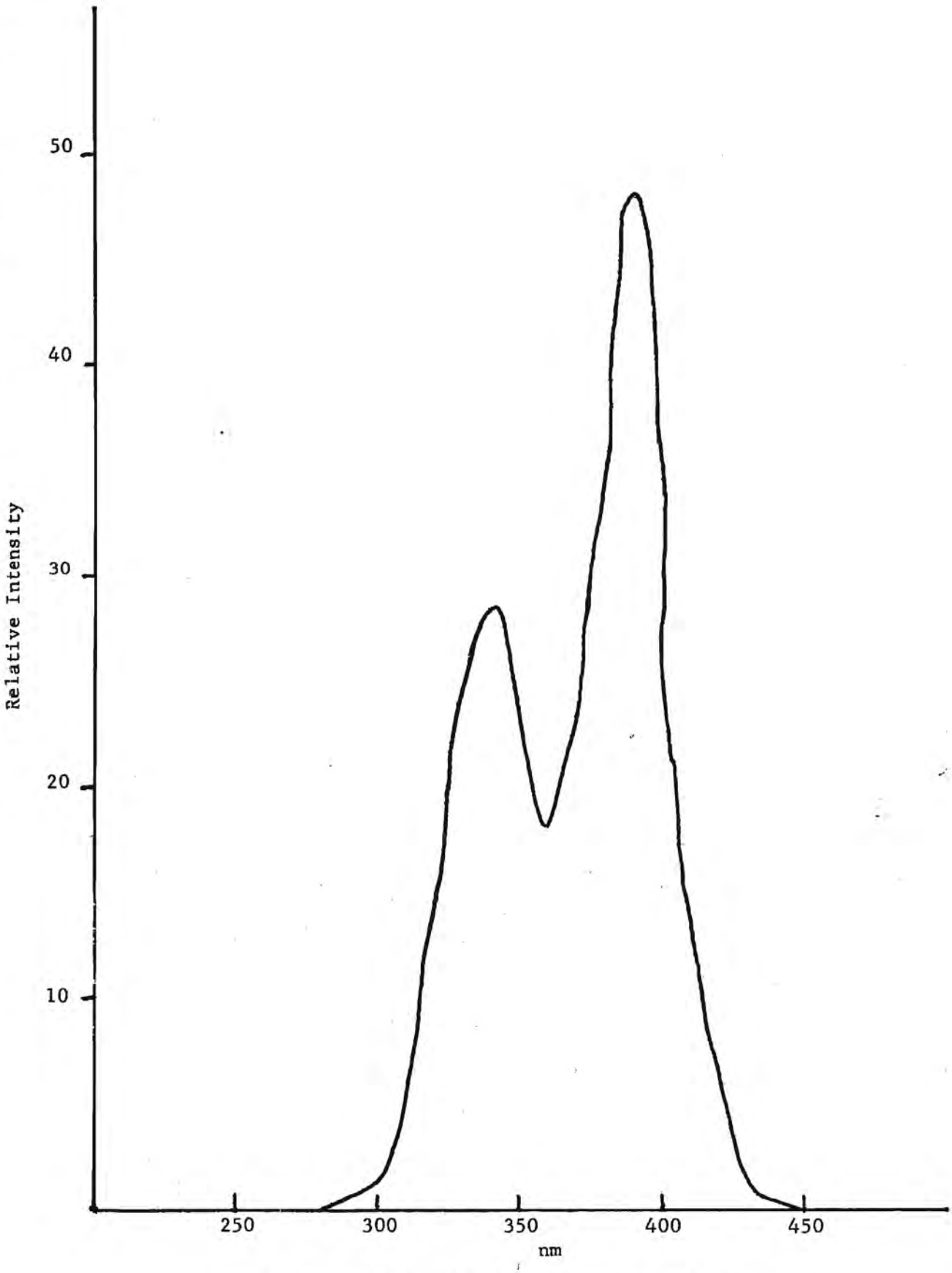


Figure 2 - Absorption Spectrum of Uvitex RBNAD

E-27-623

Monthly Progress Report Number 3

(Aug. 26, 1974 - Sept. 26, 1974)

Development of Ultraviolet Protection Nomex

Life Support SPO
Air Force Systems Command
Aeronautical Systems Division
Wright-Patterson Air Force Base, Ohio 45433

(Prepared Under Contract No. F33657-74-C-0716
by
Georgia Institute of Technology
Atlanta, Georgia 30332
W. C. Tincher, author)

SUMMARY

The computer literature search is essentially complete. A compilation of the important references will be included in the October Monthly Report.

An extensive discussion has been held with the manufacturer of Nomex on results of their studies on Nomex light stability. These discussions will provide valuable guidance in conduct of the present investigation.

Major effort this month has been directed to selection and checking of test methods for Nomex samples and to development of procedures for addition of stabilizer components to Nomex yarns.

TABLE OF CONTENTS

I. Introduction

Major effort has been directed this month toward development of procedures for addition of stabilizers to Nomex yarn. The literature survey has been essentially completed with no other major articles of interest uncovered. Testing procedures for Nomex have been checked out and initial exposure experiments are underway.

II. Literature Survey

The computer literature search with the expanded descriptor list is essentially complete. A list of the most pertinent references will be compiled and included with the next monthly report. No references to Nomex light stability in addition to those discussed in previous monthly reports have been uncovered. Computer search of the current literature will continue as each issue of Chemical Abstracts is published.

III. Technical Disccusion

As indicated in the second monthly report Dupont, manufacturer of Nomex yarn agreed to share results of some of their research work on Nomex light stability. An extensive discussion was held this month with Mr. Steven Dombchik, Supervisor in Dyes, Technical Section. Although the work related more directly to dye light-fastness the conclusions and results will have important implications in the current project. Some important conclusions are given below:

1. Photodegradation is characteristic of all aromatic polyamides. Extensive structural modification do not prevent degradation.

2. Nomex is a very strong absorber between 350 and 400 mm. The quantum efficiency for degradation is low (10^{-4} to 10^{-5}) The process is a non-chain reaction and it is not auto-catalytic.

3. Oxygen is necessary for degradation. The uptake of oxygen is linear with time if light intensity is constant. Normal free radical scavengers and antioxidants are not effective stabilizers.

4. UV screening agents are partially effective.

5. A number of conventional mechanisms have been considered:

   a.) formation of aminobenzophenone (by Photo-Fries reaction)

   b.) Photohydrolysis and oxidation

   c.) Formation of phenozine

   d.) Tautomeric shift these cyclization across C=N bonds

None of these mechanisns is completely satisfactory. The possibility of oxygen in the first excited singlet state being important in the mechanism has also been considered. Again the evidence is not conclusive.

The Dupont work suggests that, with the exception of UV screening agents, conventional light stabilizer systems may not be effective on Nomex.

IV. Techniques for Addition of Stabilizers to Nomex

In order for a stabilizer to be effective, it must be incorporated in the fiber or in a resin used in finishing. Little is known concerning the incorporation of various materials in Nomex except what is available in the published dyeing technology. This information is confined to recommended procedures for the application of cationic dyes. Since the types of materials being considered a stabilizers include both ionic and non-ionic materials, initial studies will include the application of selected dyes from several classes of dyes by techniques and under conditions recommended for cationic dyes to learn more concerning the relationship between structural features of dyes and their substantivity to and diffusion in the fiber. These experiments are being carried out both in the presence and absence of a suitable plasticizer for the fiber to promote diffusion in the fiber. Based on the results obtained commercially available stabilizers (UV screens, antioxidants, UV stabilizers, fluorescent brighteners) will be applied to the fiber using conditions for their application which would be predicted to promote reasonable sorption and degree of fiber penetration.

Based on the structure of many commercially available stabilizers, it it is expected that their diffusion will be the limiting factor in sorption due to the molecular size of the stabilizers. Another approach is to produce is to produce the stabilizer in-situ, that is, the two (or more) chemicals necessary for forming the stabilizer are applied to the fiber stepwire, the

reaction between the stabilizer precursor molecules taking place in the fiber. Here again, this technique has been used successfully in dyeing fibers, particularly where diffusion is a problem. An example of such a process is the formation of insoluble metal salts or metal chelates in the fiber, such materials acting as stabilizers. Attempts to accomplish this will parallel the study of the sorption of commercial stabilizers.

All of the work described above is being carried out on small skeins of Nomex yarn (2.5g) using the Atlas High Temperature Launder-O-Meter. This will provide sufficient treated fiber for light exposure and tensile tests.

V. Testing Procedures

A check on the selected testing procedures for Nomex yarn has been carried out.

One package of 200 denier Nomex yarn was tested for tenacity and elongation using ASTM method D 2256, option 1. Time to break was 20 $\pm$ 3 seconds. Each specimen was twisted 7.8 turns per inch prior to testing, as directed by note 4 of D 2256, which recommends,

$$\frac{110 \pm 10}{\sqrt{\text{denier}}} \quad \text{turns per inch}$$

Sufficient tests were made to detect a significant difference in tenacity and elongation of $\pm$ 2.0 percent. Denier was measured following ASTM method D 1970.

Results obtained were as follows:

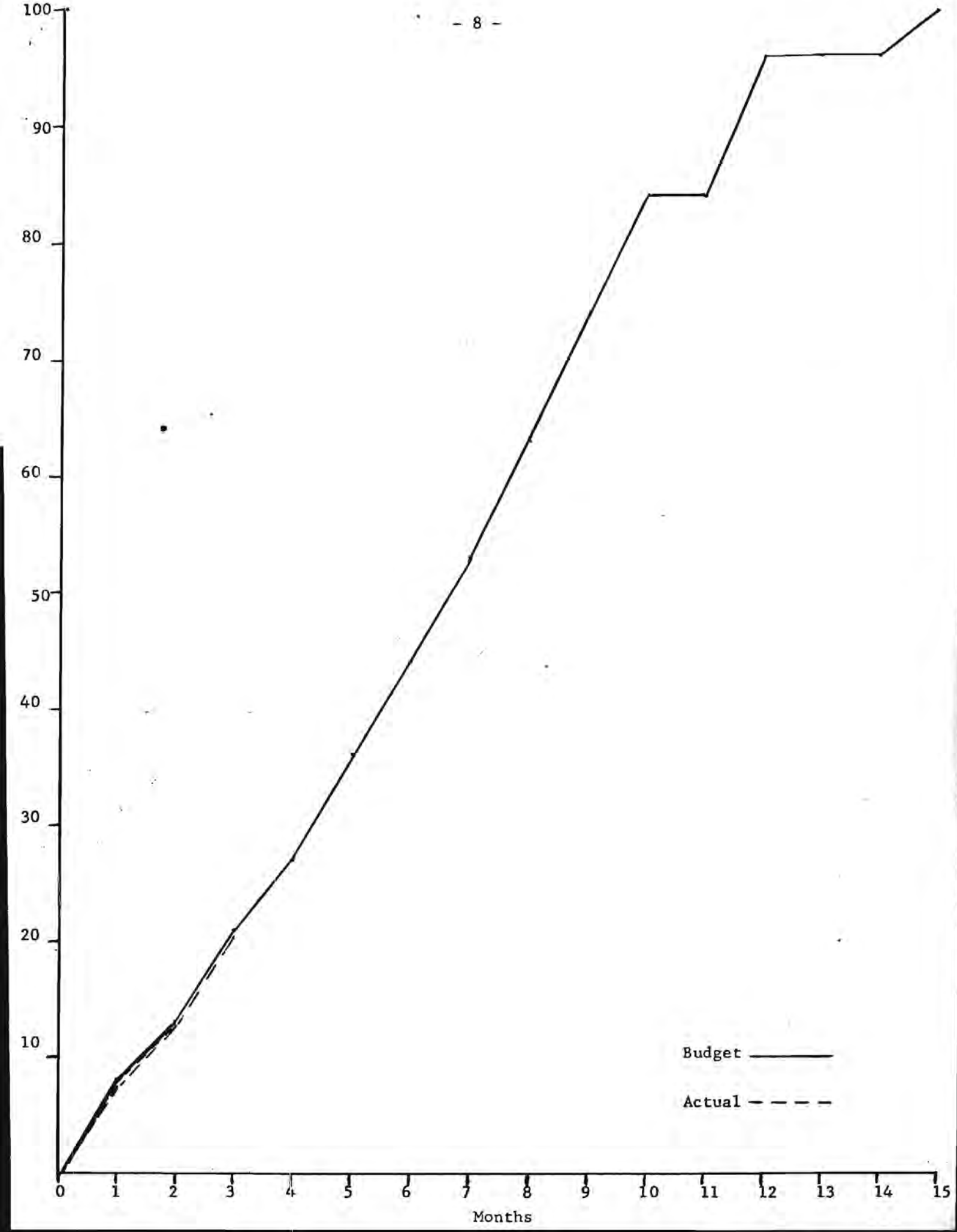
Average Tenacity, grams/denier	5.15
Average Elongation, %	57.2
Tenacity Variation, % CV	4.3
Elongation Variation, % CV	4.1
Average Denier	207

VI. Future Work

Initial exposure experiments are underway. Samples containing stabilizers will be prepared and tested this month. Systems containing light screening agents will be selected for the first experiments.

VII. Budget

The funds budgeted and either expended or allocated for the first three months are shown on the attached graph.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E-27-623

Monthly Progress Report Number 4

(Sept. 26, 1974 - Oct. 26, 1974)

Development of Ultraviolet Protection Nomex

Life Support SPO
Air Force Systems Command
Aeronautical Systems Division
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Summary

The computer literature search has been completed and the results of the survey are appended to this report. A total of 958 citations were examined and approximately 175 have been selected for inclusion in the appendix. References to thermal degradation, ultraviolet degradation, and stabilization of both alphatic and aromatic polyamides have been included.

Procedures have been developed and tested for incorporation of selected stabilizers in Nomex fiber. Five ultraviolet screening agents which have strong absorption bands in the UV region responsible for Nomex degradation have been successfully applied to the fiber and specimens for UV exposure testing are being prepared.

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I. Introduction

Major efforts this month have been directed toward completion of the literature survey and toward continued development of procedures for incorporation of stabilizers in Nomex fiber. Techniques for incorporating both ionic and non-ionic materials in Nomex have been developed and can be used for addition of stabilizers to Nomex. Initial studies on changes in Nomex yarn properties on exposure to both the carbon-arc and xenon-arc lamps have been carried out and results are reported.

II. Literature Survey

The computer search of Chemical Abstracts from July, 1968, to June, 1974, has been completed using the list of descriptors shown in Table 1. The computer listed 958 citations of which 172 were selected for inclusion in the bibliography shown in the Appendix. Many references to new aromatic amide compositions showing improved thermal stability and references to the more prosaic and standard stabilizers for thermal degradation of aliphatic amides were not included in the list as these subjects are less pertinent to the present work. The selected references have been divided into 12 categories

TABLE 1.

DISCRIPTOR LIST NOMEX DEGRADATION SEARCH

Group	Term No.	Term
G001	1	Nomex
G001	2	Aramid
G001	3	Poly(1,3-Phenylene Isophthalamide)
G001	4	Poly(1,4-Phenylene Terephthalamide)
G001	5	Poly(1,3-Phenylene Terephthalamide)
G001	6	Poly(1,4-Phenylene Isophthalamide)
G001	7	Poly(4-Aminobenzoic Acid)
G001	8	Poly(3-Aminobenzoic Acid)
G001	9	Kevlar
G001	10	Fiber B
G001	11	HT-1
G001	12	HT-4
G001	13	PRD 49
G002	14	Aromatic*
G002	15	Arom
G002	16	*Benz*
G002	17	*Isoquino*
G002	18	*Indol*
G002	19	*Iden*
G002	20	*Indazol*
G002	21	*Indanyl*
G002	22	*Fluoren*
G002	23	*Phenyl*
G002	24	*Phthal*
G002	25	*Tolyl*
G002	26	*Pyridyl*
G002	27	*Naphythyl*
G002	28	*Aryl*
G002	29	*Anthryl*
G002	30	Arene*
G003	31	Poly*
G003	32	Macromol*
G003	33	Macro-mol*
G004	34	*Amide*
G005	35	UV
G005	36	U.V.
G005	37	U. V.
G005	38	Ultraviolet
G005	39	Ultra-violet
G005	40	Light
G005	41	Decompos*
G005	42	Decompn
G005	43	Degrad*
G005	44	Degrdn
G005	45	Breakdown*
G005	46	Break-down*
G005	47	Breaking Down*
G005	48	Unzip*
G005	49	Cleav*
G005	50	*Stabil*
G005	51	*Stable*
G005	52	Deteriorat*
G005	53	Degenerat*
G005	54	Reaction
G005	55	Depolymeriz*
G005	56	Depolymn
G005	57	Hydroly*
G005	58	Solvoly*
G005	59	Photoly*
G006	60	Heat
G006	61	Thermal*
G006	62	*Flam*
G006	63	Fire*
G007	64	Resist*
G007	65	*Proof*
G007	66	*Retard*
G008	67	Nylon*
G009	68	High Temp*
G009	69	Nonflammable
6009	70	Non-flammable
6010	71	Kynol
6010	72	Polybenzimidazole
6010	73	Poly(Benzimidazole)
6010	74	PBI
6010	75	P.B.I.
6010	76	P. B. I.

A. General Papers on UV Degradation

B. UV Degradation of Nylon 6 and Nylon 6,6

C. Thermal Degradation of Nylon 6 and Nylon 6,6

D. Thermal Stabilizers for Nylon 6 and Nylon 6,6

E. UV Stabilizers for Nylon 6 and Nylon 6,6

F. Thermal Degradation of Aramids

G. UV Degradation of Aramids

H. Thermal Stabilizers for Aramids

I. UV Stabilizers for Aramids

J. Dyeing of Aramids

K. Stability and Degradation of Phenolic Fibers

L. Photochemistry of the Amide Bond

In the important area of UV stabilizers for Aramids only three references were discovered. The reported stabilizers are Tinuvin P and Cu^{+2}. The literature, therefore, provides little guidance in selection of compounds for Nomex stabilization.

Eight references have been found that discuss the mechanism of radiation and UV degradation of Nomex and other aramids. These references will be useful in selection of some materials for screening studies.

III. Addition of Stabilizers to Nomex

The types of materials being considered as possible stabilizers for Nomex include both ionic and non-ionic materials. Little is known concerning the incorporation of such materials in Nomex except the information which is available in published technology for the application of cationic dyes. Initial studies, therefore, have included the application of selected dyes from several classes of dyes under conditions similar to those used in the application of cationic dyes to discover the relationships between structural features of dyes and their substantivity to and diffusion in the fiber.

In all of the literature concerning the dyeing of Nomex high concentrations of dye carriers are required at dyeing temperatures higher than 212°F. Many carriers have been evaluated for the application of cationic dyes[1]. Those recommended include benzaldehyde[2] (for Nomex E8, a fiber chemically modified for dyeing with cationic dyes), acetophenone[3] and benzyl alcohol[4] for Nomex type 450. duPont's published recommendations for dyeing Nomex type 450 include the use of acetophenone (40 g/l) at a dyeing temperature of 250°F. Conversations with Dr. P. G. Noble and Richard Hunt of Tootal Limited, Manchester, England, revealed that they had successfully dyed Nomex with cationic dyes using benzyl alcohol[4]. A British patent which describes this process has been issued to Tootal. In their work it was discovered that important factors in the light stability of cationic dyes on Nomex were the purity of the dyes, and the type and purity of surfactants used for emulsification of the carrier.

duPont makes no recommendation for the dyeing of Nomex type 430; however, they report that it has been dyed successfully following the teachings of U.S. Patent 3,771.949[5]. This dyeing process is very complicated requiring pretreatments of the fiber with high boiling liquids such as ethylene glycol, propylene glycol, tetraethylene glycol, and their alkyl derivatives at temperatures of approximately 190°C followed by application of cationic dyes in solvent mixtures consisting typically of such solvents as dimethylacetamide, dimethylformamide, and dimethyl sulfoxide.

Fabrics made from Nomex type 430 dyed using procedures recommended for Nomex type 450 are unsatisfactory due to streakiness and lack of penetration of the dye into the fiber. The following types of dyes have been applied to Nomex type 430 at 250°F using the carrier, benzyl alcohol, at concentrations up to 100g/1:

Leveling acid

Neutral dyeing acid

Disperse

Cationic

In all cases, 5.0% dye based on fiber weight was used. Medium depths of shade were obtained with disperse, cationic, and neutral dyeing acid dyes when the concentration of carrier was 100g/1. Propylene carbonate was ineffective as a carrier under the same dyeing conditions. The dyeing results with benzyl alcohol were convincing evidence that anionic, cationic, and non-ionic materials can be incorporated in the fiber.

The first group of stabilizers to be investigated are referred to as optical brighteners. It has been shown that these materials absorb strongly in that region of the ultra-violet which is responsible for the degradation of Nomex. Some brighteners are non-ionic, some anionic. The ten (10) brighteners listed below were applied to the fiber at 250°F in the presence of benzyl alcohol.

Optical Brighteners

Sandoz

Leucophor PAB - anionic - stilbene derivative

Leucophor PC - anionic

Leucophor EFR - non-ionic

Eastman Chemical Products

Eastman OB-1 - non-ionic

General Aniline and Film Corporation

Blancophor AW

Ciba - Geigy

Uvitex NFW - Anionic

Uvitex WGS - nonionic - coumarine derivative

Uvitex CF - Anionic

Uvitex RBNAD - Anionic - stilbene derivative

Uvitex 4BMA - Anionic - stilbene derivative

Based on the intensity of fluorescence of the treated fibers as observed under ultra-violet light, it is concluded that several of the brighteners are substantive to the fiber:

Highly fluorescent -

Uvitex WGS

Blancophor AW

Uvitex RBNAD

Leucopher EFR

Moderately fluorescent -

Uvitex NFW

Stability studies will be made on the fibers containing these brighteners.

IV. Results of Initial Exposure Experiments

Samples of Nomex type 430 have been exposed to the carbon -arc and xenon -arc lamps in the Fade-Ometer for 100 hours. Tensile strength and elongation were determined at 20 hour intervals for the exposed samples. Results of these experiments are shown in Figures 1 and 2. It is apparent from these data that exposure to the carbon-arc gives much more rapid deterioration in the properties of Nomex. The carbon -arc has very intense bands of radiation between 350 and 425 mm.[6] This intense output corresponds directly with the wavelengths of energy responsible for Nomex degradation. The carbon -arc exposure is therefore probably more severe than outdoor exposure in degradation of Nomex. Xenon -arc exposure probably compares more favorably with outdoor exposure. The

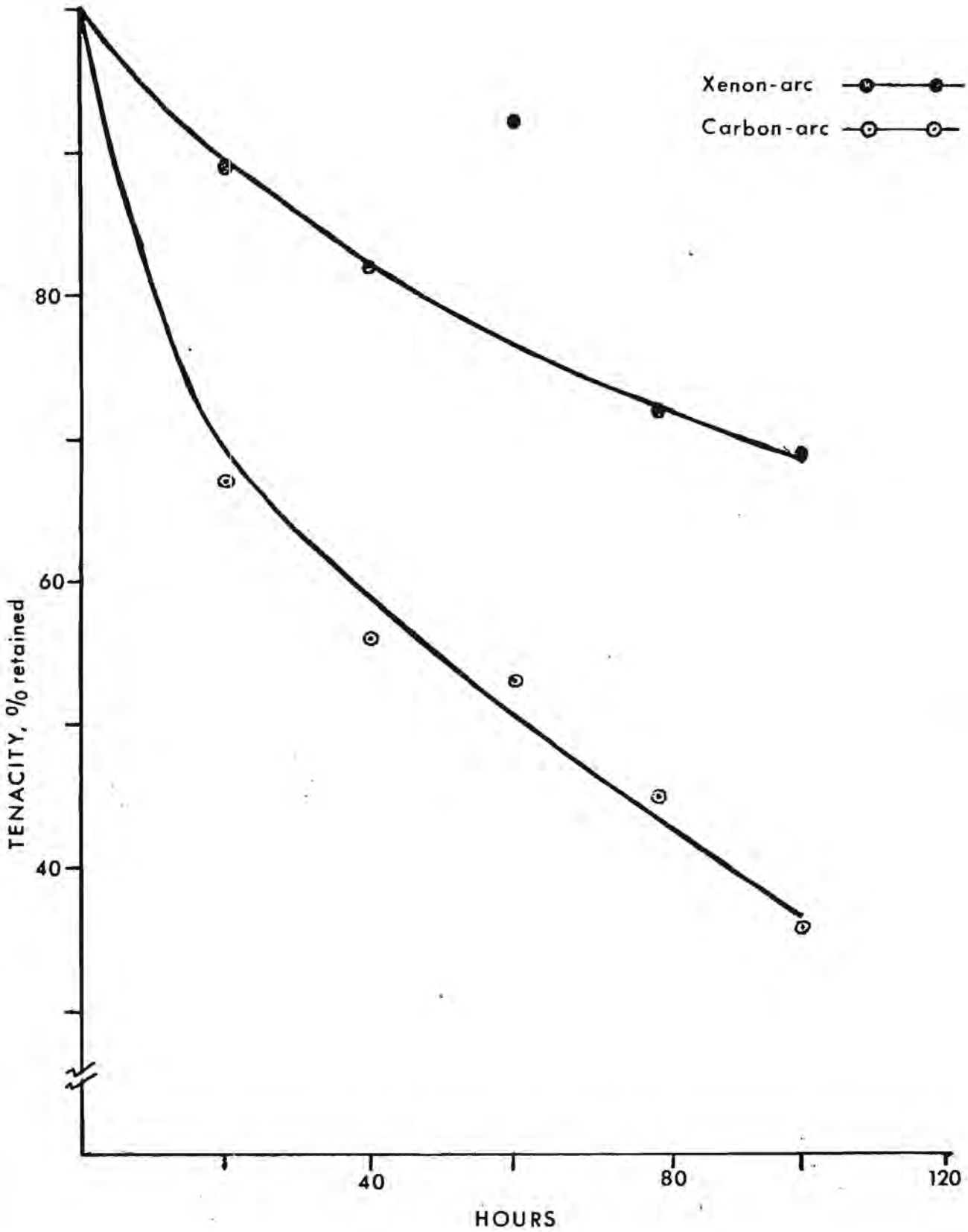
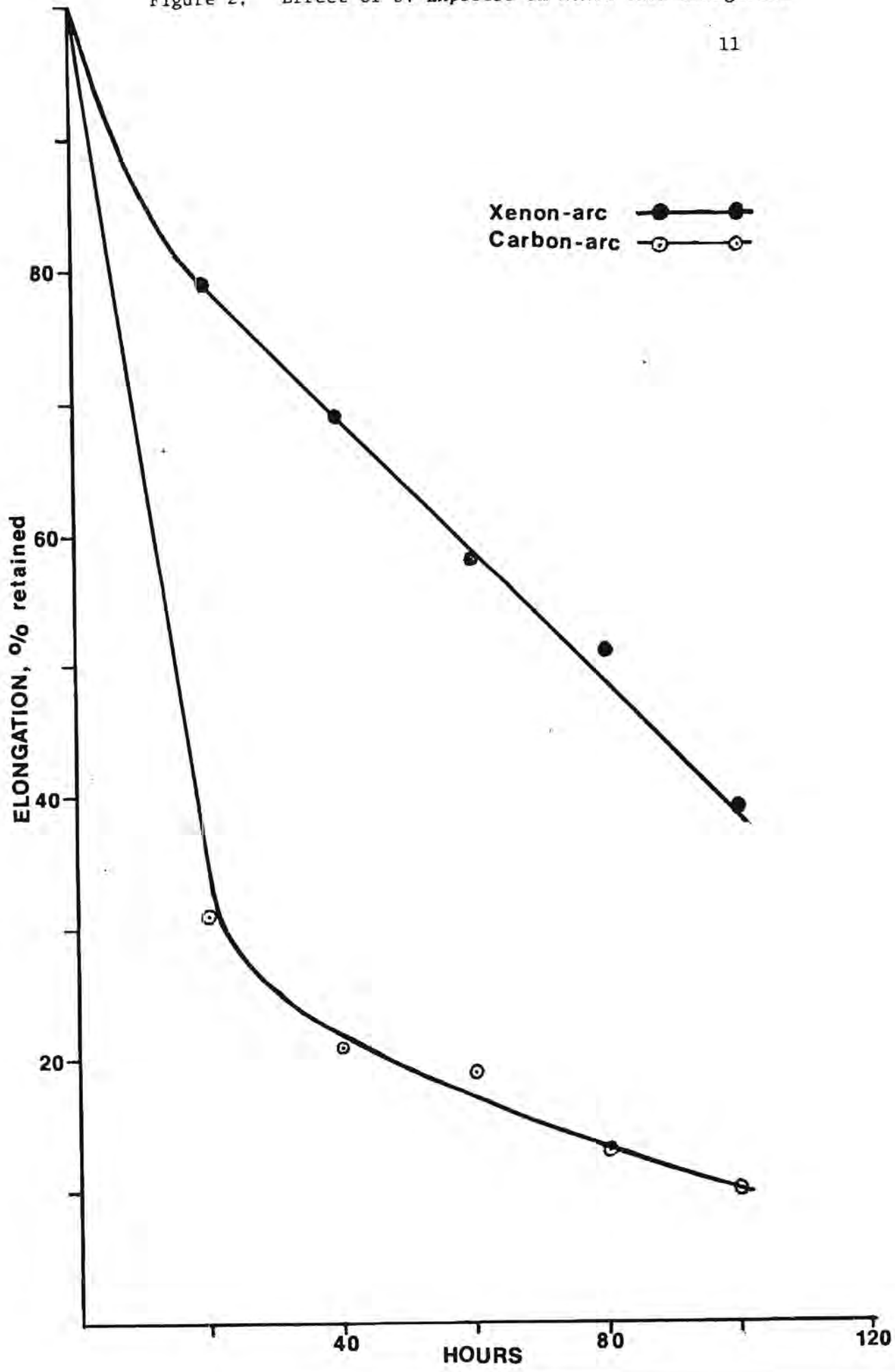


Figure 1. Effect of UV Exposure on Nomex Yarn Tenacity

Figure 2. Effect of UV Exposure on Nomex Yarn Elongation



results also clearly indicate that the fiber elongation is more severely affected than the tenacity on exposure to UV radiation.

Similar exposure experiments are almost completed for Nomex Type 433.

V. Additional Effort Related to Nomex Degradation

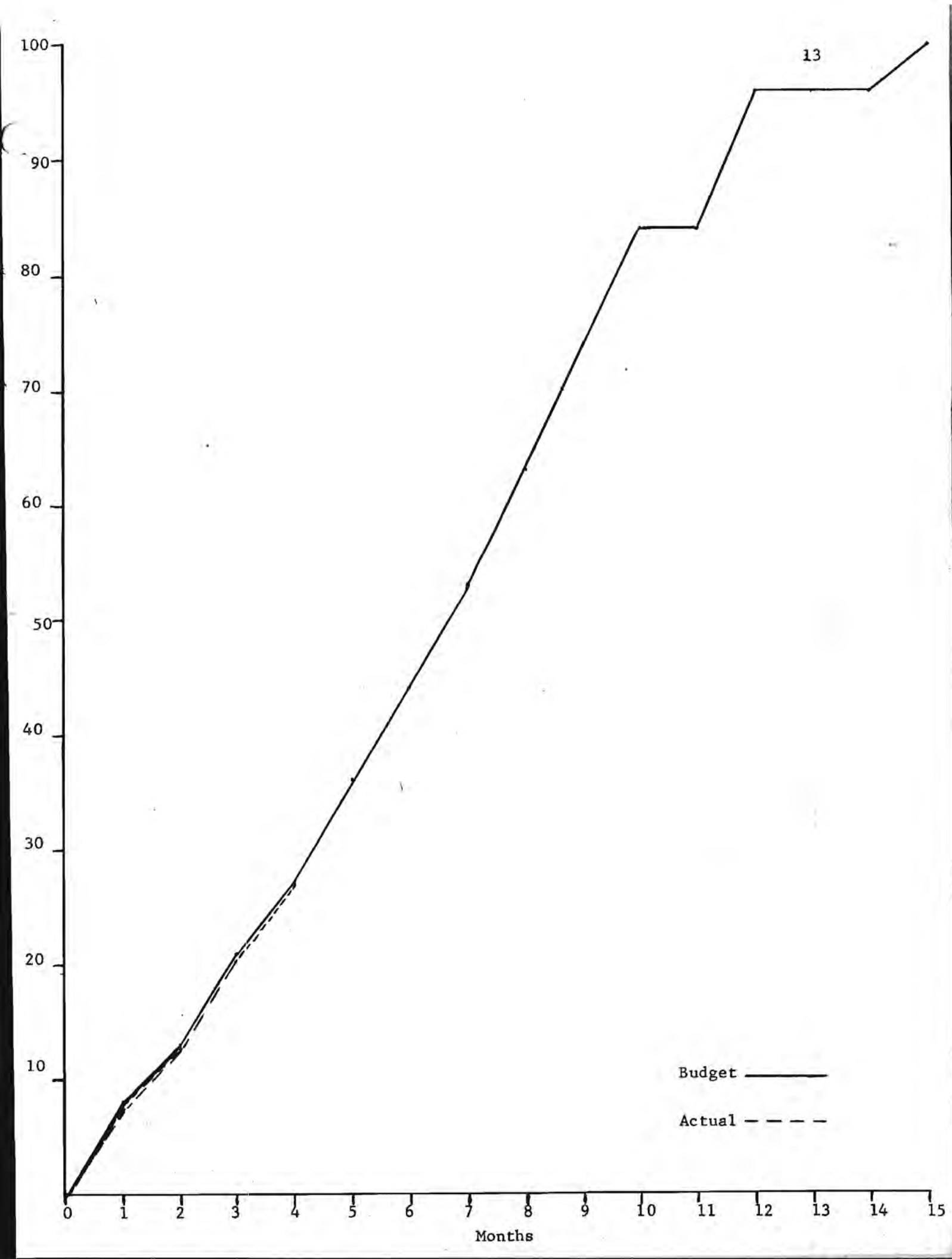
In addition to the work on stabilizers for improving the resistance of Nomex to UV degradation, studies have begun on the basic reactions involved in aromatic amide photodegradation. This work is being carried out at no cost to the Air Force as part of the regular educational and research activities of the Georgia Tech School of Textile Engineering. These studies will involve extensive use of aromatic amide model compounds to elucidate the fundamental degradation reaction mechanisms and should provide some guidance in the selection of stabilizer systems.

VI. Future Work

Samples of Nomex containing five difference screening agents have been prepared and will be exposed and tested. Samples containing other selected stabilizers will be prepared.

VII. Budget

The funds budgeted and either expended or allocated for the first four months are shown on the attached graph.


100
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80
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1
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15
Months
Budget
Actual

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E-27-629

Monthly Progress Report Number 5

(Oct. 26, 1974 - Nov. 26, 1974)

Development of Ultraviolet Protection Nomex

Life Support SPO
Air Force Systems Command
Aeronatucial Systems Division
Wright-Patterson Air Force Base, Ohio 45433

(Prepared Under Contract No. F33657-74-C-0716
by
Georgia Institute of Technology
Atlanta, Georgia 30332
W. C. Tincher, author)

Summary

Five ultraviolet screening agents which have strong absorption bands in the UV region responsible for Nomex degradation have been successfully applied to Nomex fiber. Testing of three of these samples by exposure for 100 hours in the Xenon arc Fade-Ometer has been completed. One of the stabilizer candidates shows some promise for reduction of the property loss of Nomex on UV exposure.

Studies have continued on techniques for incorporation of stabilizers in Nomex. Emphasis has been directed this month toward materials capable of complexing metal ions which may act as stabilizers and on techniques for incorporation of sulfur containing stabilizers in Nomex yarn. Samples for testing are now being prepared.

TABLE OF CONTENTS

I. Introduction

Efforts this month have been directed toward preparation and testing of samples containing UV screening agents. Five screening agents have been applied to Nomex by the dyeing procedures reported last month and testing is complete on three of these samples. Uvitex WFS, a fluorescent brightening agent, shows some promise as a screening agent for Nomex.

Several new procedures for incorporation of stabilizers have also been investigated this month to develop techniques for incorporation of sulfur and metal ion containing stabilizers in Nomex.

II. Results of Exposure Experiments on Nomex Types 430 and 433

Samples of Nomex types 430 (white) and 433 (sage green) have been exposed to the carbon-arc and xenon-arc lamps in the Fade-Ometer for 100 hours. Tensile strength and elongation were determined at 20 hour intervals for the exposed samples. The per cent retention of tenacity and elongation as a function of exposure time is shown in Figures 1 and 2. It is apparent from these results that the rate of degradation of the Type 430 (white) Nomex is much greater than rate for Type 433 (sage green) for both exposure sources. The results also clearly indicate that the fiber elongation is more severely affected than the tenacity in both xenon and carbon-arc exposure.

As reported earlier, duPont is adding a UV stabilizer to Type 433 Nomex. This stabilizer may be contributing to the improved property retention for this type Nomex. The green pigment in Type 433 may also be contributing to the improved UV resistance.

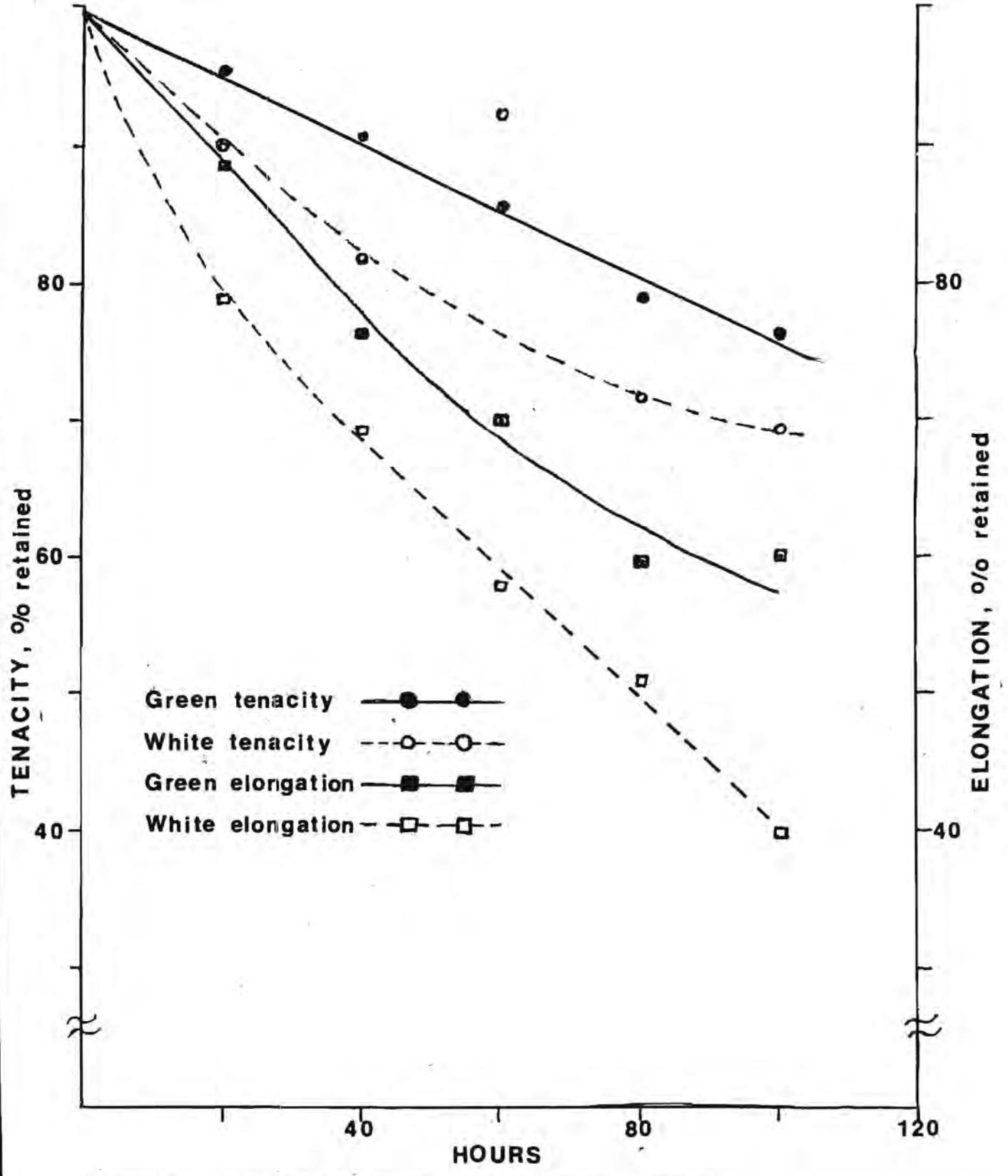


Figure 1. Retention of tenacity and elongation of Nomex Type 430 (white) and Type 433 (sage green) after Xenon-arc exposure

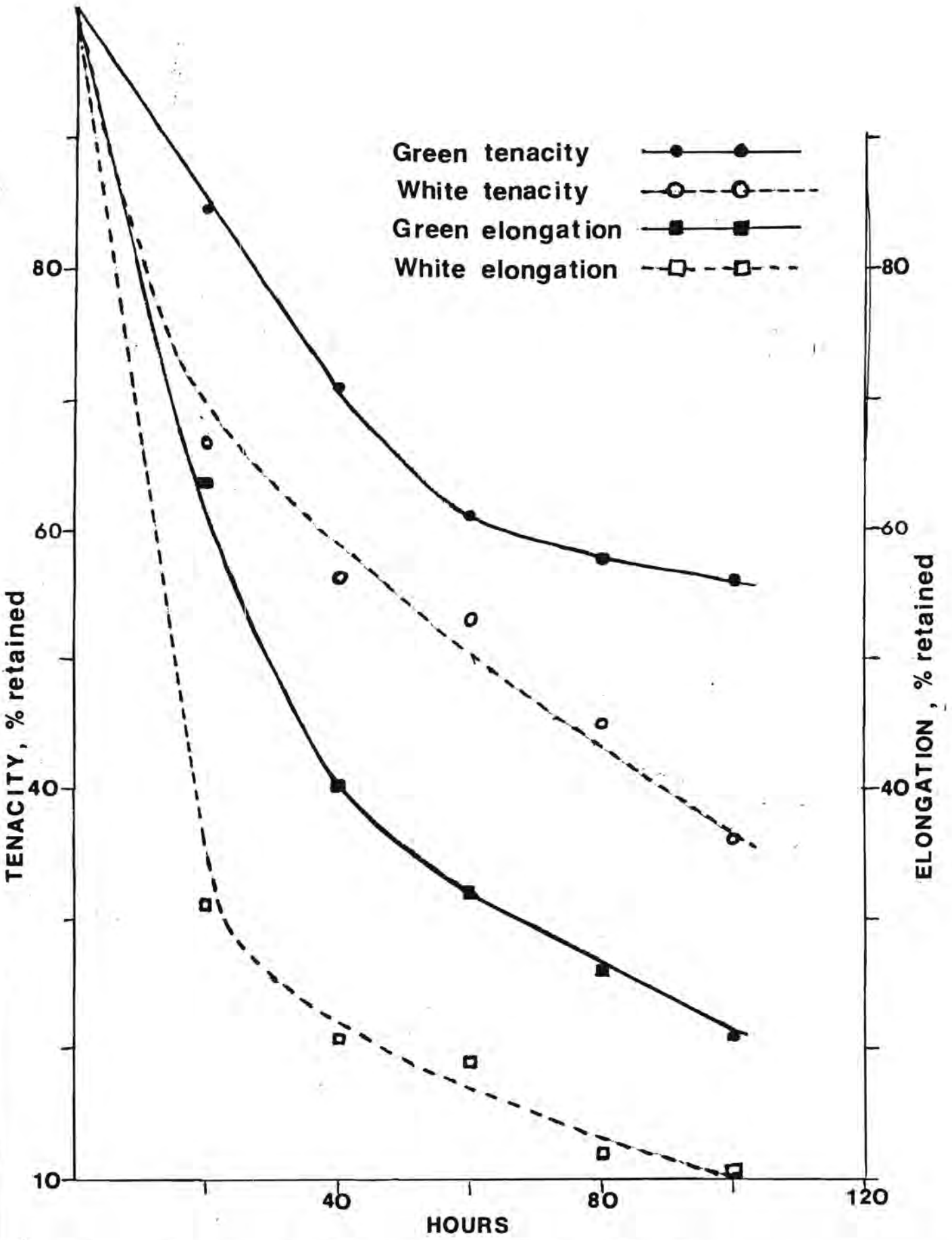


Figure 2. Retention of tenacity and elongation of Nomex Type 430 (white) and Type 433 (sage green) after Carbon-arc exposure

III. Addition of Stabilizers to Nomex

Work has continued to discover other materials which can be used as either carriers for facilitating the incorporation of stabilizers in Nomex or which may themselves serve as the basis for a stabilizer system for the fiber.

Acetophenone is recommended by duPont as a carrier for dyeing Nomex 450. It has been discovered that Chemocarrier FPN, a compounded carrier composition reported to be based on acetophenone (Tanatex Corporation), is effective in applying cationic and disperse dyes to Nomex. The concentration of the carrier required is 40 g/l at a dyeing temperature of 250-260° F.

Other materials which have been investigated include salicylic acid and o-benzoic sulfimide. They were chosen because it was thought that they may be effective carriers due to the fact that they are both small molecules possessing high dipole moments. In addition, they are also capable of forming complexes with metal ions which could serve as stabilizers for Nomex. Dyeing studies using these materials show that both materials provide some carrier action, salicylic acid being more effective than o-benzoic sulfimide. Quantitative measurements will be made to determine the substantivity of these materials to Nomex.

It has been reported that sulfur dyes have a light stabilizing action on aromatic polyamides and thiourea has been suggested as a light stabilizer for dyes. An attempt has been made to incorporate this material is Nomex by a padding-thermofixation process (200°C). The amount of thiourea absorbed is being determined using the election microprobe technique.

Oxidation of thiourea results in the formation of compounds possessing the disulfide link and also elemental sulfur, both of which may act to stabilize the fiber by a free radical scavenging mechanism.

IV. Stabilizer Screening Studies

The first group of stabilizers to be investigated are optical brighteners. These materials absorb very strongly in the region of the ultraviolet which is responsible for Nomex degradation. Five of these materials have been applied to Nomex yarn by "dyeing" procedures reported last month. The optical brighteners selected were:

Uvitex WGS
Blancophor AW
Uvitex RBNAD
Leucophor EFR
Uvitex NFW

Xenon-arc exposure and testing have been completed on samples containing three (3) of these screening agents - Leucophor EFT, Uvitex NFW, and Uvitex-WGS.

The per cent retention of tenacity and elongation for Nomex containing Leucophor EFR compared to a control sample are shown in Figure 3. The sample containing the additive shows a significantly greater loss of both tenacity and elongation than the control sample. Thus, it appears that some materials do have the capability of sensitizing Nomex degradation. This result is important in that it demonstrates that the degradation mechanism can be altered by chemical additives.

Similar results for Nomex yarn containing Uvitex NFW are shown in Figure 4. These data suggest that little change in either tenacity or elongation retention has resulted from the addition of this material.

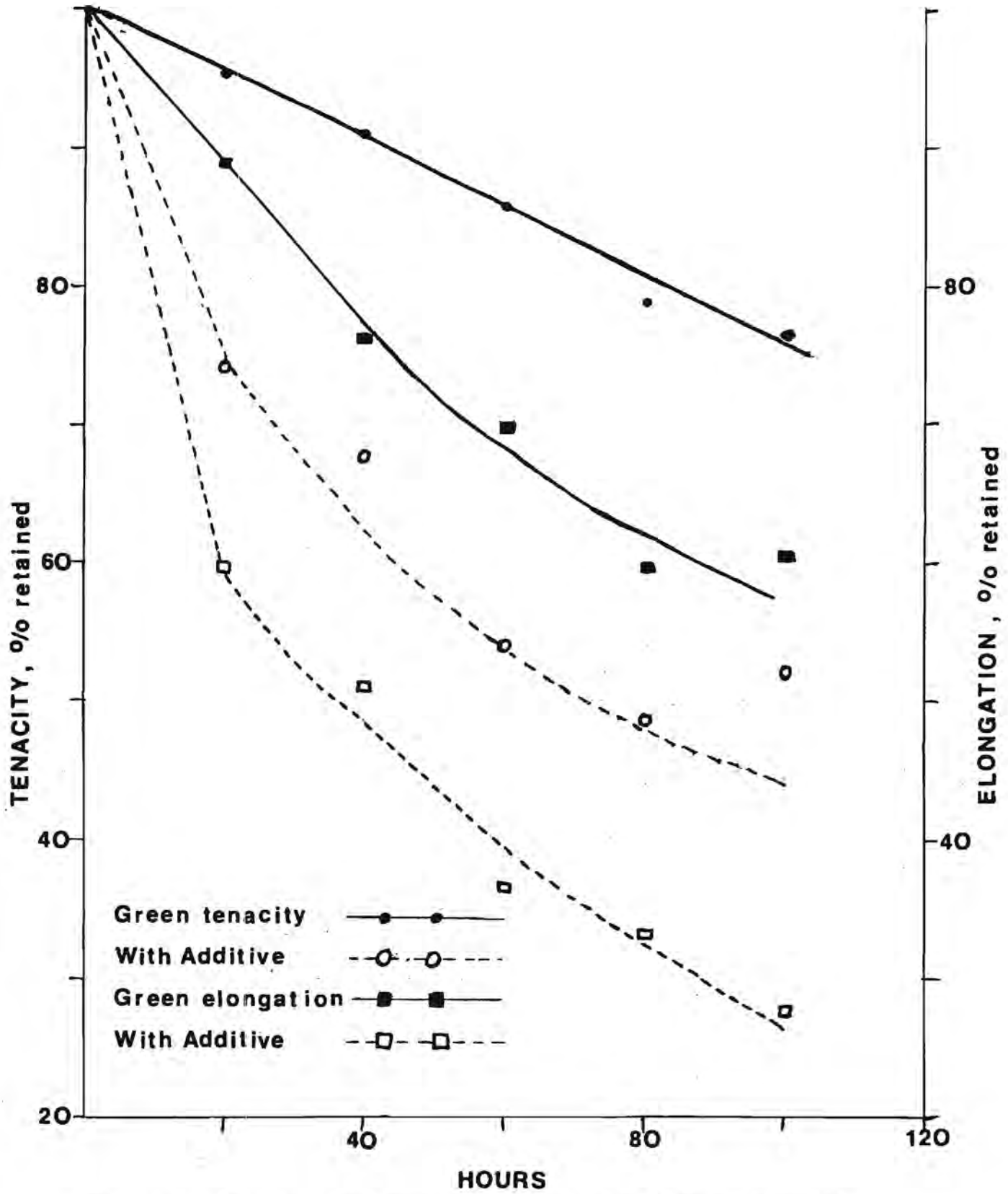


Figure 3. Retention of tenacity and elongation of Nomex Type 433 containing Leucophor EFR compared to control sample after Xenon-arc exposure

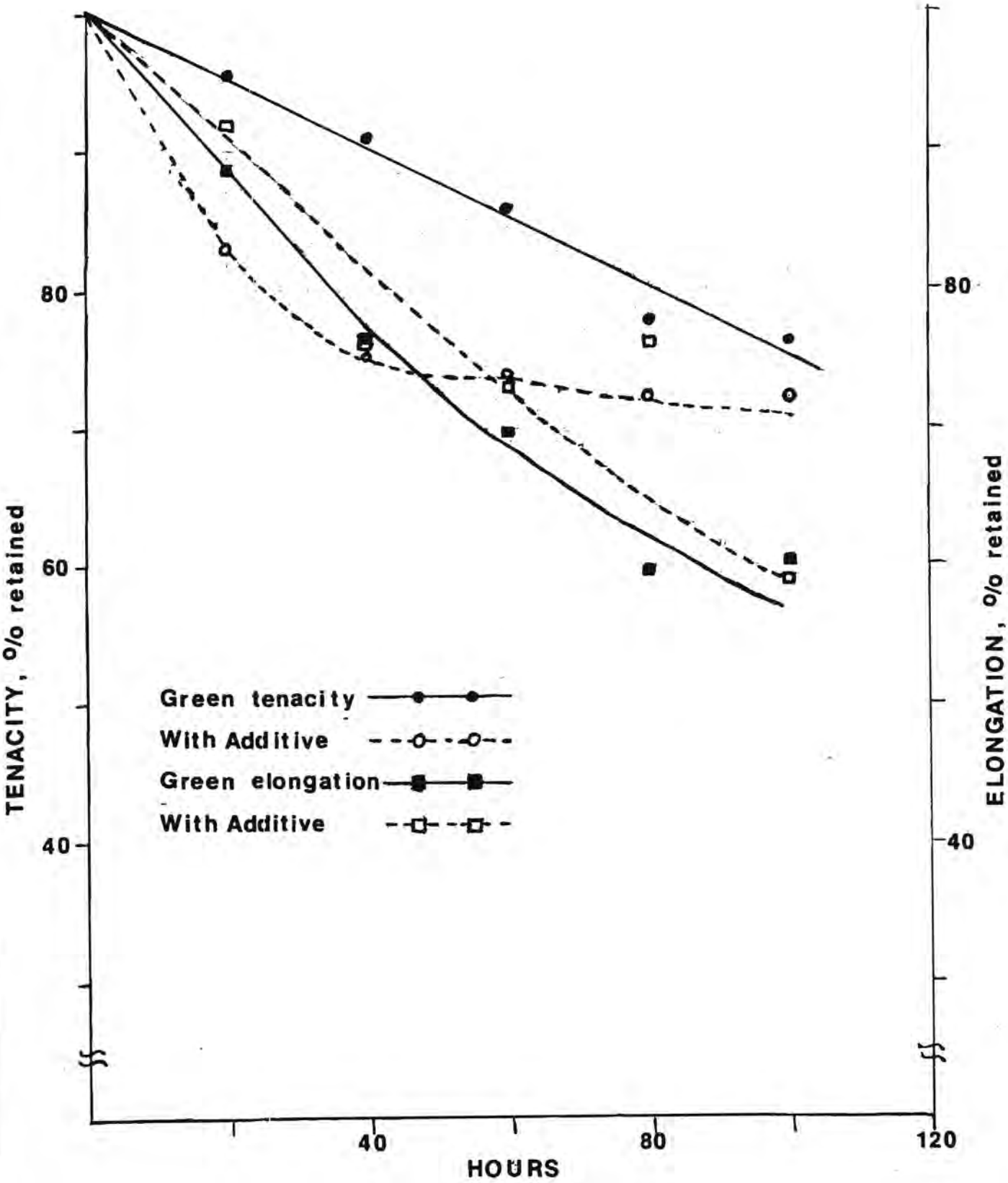


Figure 4. Retention of tensity and elongation of Nomex Type 433 containing Uvitex NFW compared to control sample after Xenon-arc exposure

Tenacity and elongation retention after exposure of Nomex containing Uvitex WGS to the Xenon-arc Fade-Ometer are shown in Figure 5. This sample is particularly interesting in that initially (first 60 hours), improvement in retention of elongation is observed. A similar effect on tenacity is not observed. This effect on sample elongation by Uvitex WGS suggests that this material should be investigated in greater detail.

V. Future Work

Samples of Nomex containing other screening agents are now under test. Nomex yarn samples containing metal ion complexes and sulfur containing stabilizers will be prepared.

VI. Budget

The funds budgeted and either expended or allocated for the first five months are shown on the attached graph.

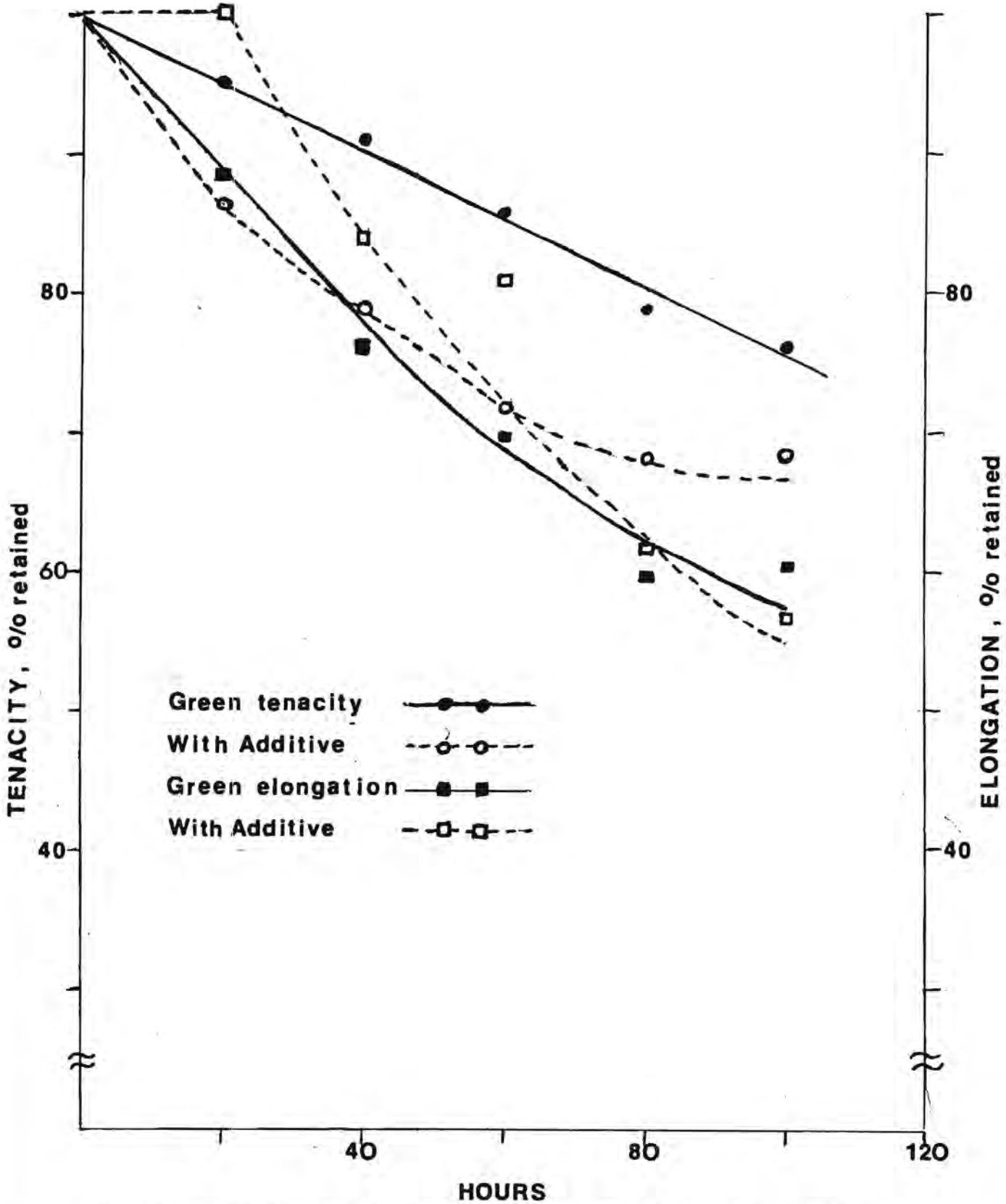
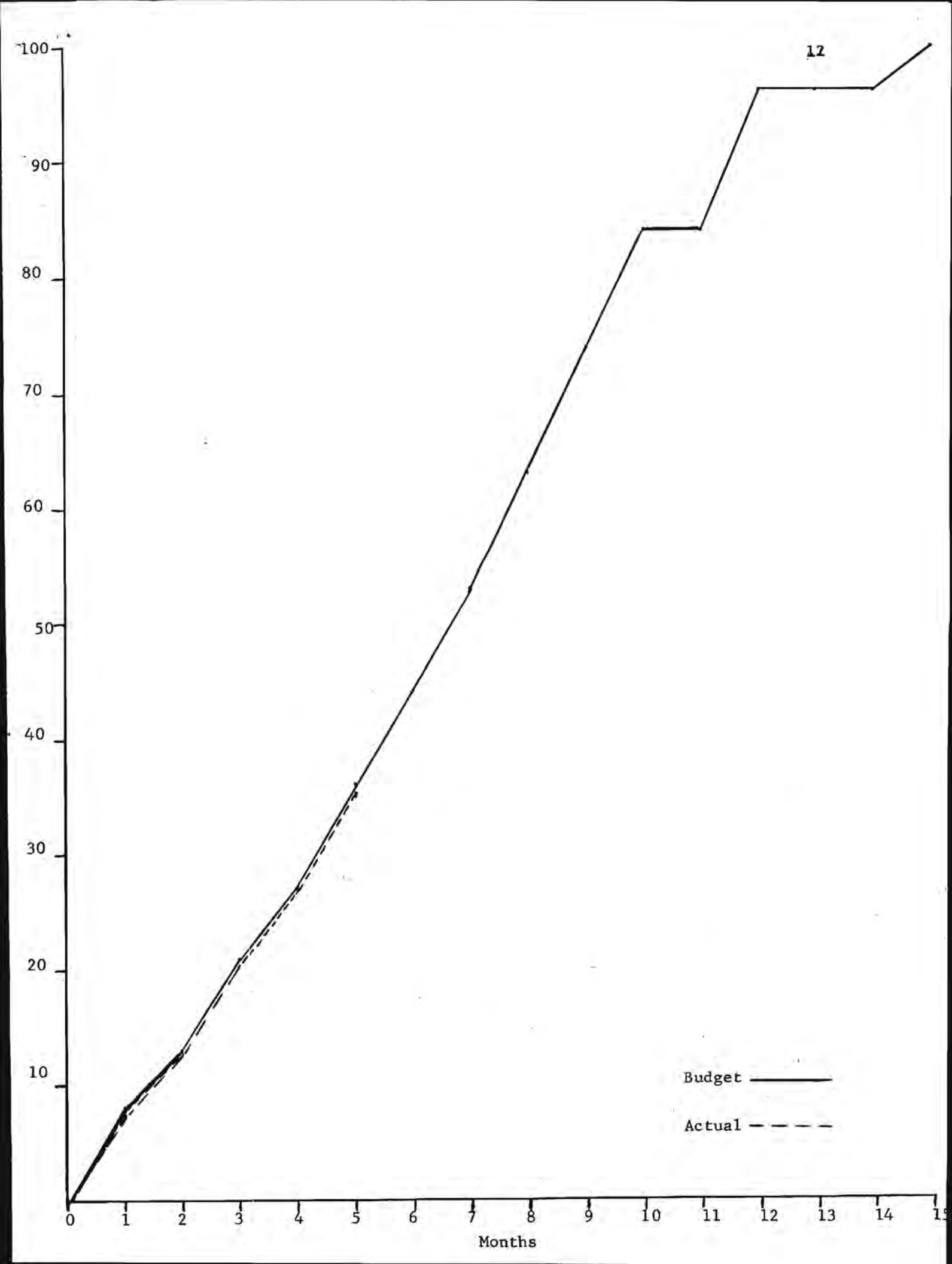


Figure 5. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex WGS compared to control sample after Xenon-arc exposure.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Months
Budget
Actual

E-27-623

Monthly Progress Report Number 6

(Nov. 26, 1974 - Dec. 26, 1974)

Development of Ultraviolet Protection Nomex

Life Support SPO
Air Force Systems Command
Aeronatucial Systems Division
Wright-Patterson Air Force Base, Ohio 45433

(Prepared Under Contract No. F33657-74-C-0716
by
Georgia Institute of Technology
Atlanta, Georgia 30332
W. C. Tincher, author)

SUMMARY

Studies are essentially complete on ultraviolet screening agents of the fluorescent brightner type for improvement in Nomex UV degradation. One compound of this type shows promise for stabilizing Nomex.

A series of sulfur containing compounds have been tested for Nomex stabilization. These compounds gave no improvement in the resistance of Nomex to UV degradation.

Experiments are now underway on metal ion containing stabilizers which "quench" intermediate excited states involved in UV degradation.

Table of Contents

I. Introduction

During this month studies have focused on fluorescent brightners and sulfur containing compounds as possible stabilizers for Nomex. Experiments on fluorescent brightners are essentially complete and a review of the data is planned for the January monthly report. One brightener, Blancophor AW, shows promise as a Nomex stabilizer.

Studies on sulfur containing compounds have been completed. These compounds show no promise for improving the light stability of Nomex.

II. Literature Survey Update

Continuous monitoring of the literature since the last report on the literature survey (Monthly Report Number 4) has yielded several recent publications related to the research project. A number of these report stabilizers for improvement of Nomex light stability (2,5,6,7). Reported stabilizers are either light absorbers of the benzotriazole type (similar to the Tinuvin series) or excited state quenchers containing nickel and sulfur or phosphorous. Compounds of these types are currently under study.

III. Studies on Fluorescent Brightenings for Nomex Stabilization

Work is essentially complete on investigation of fluorescent brightening agents as possible stabilizers for Nomex. These compounds have very high absorption peaks in the region of the spectrum that is responsible for Nomex degradation. As described in previous monthly reports, these compounds were added to Nomex sage green yarns by a dyeing procedure.

Results of exposure to both xenon and carbon - arc light sources have shown that only one of these materials, Blancophor AW, shows promise

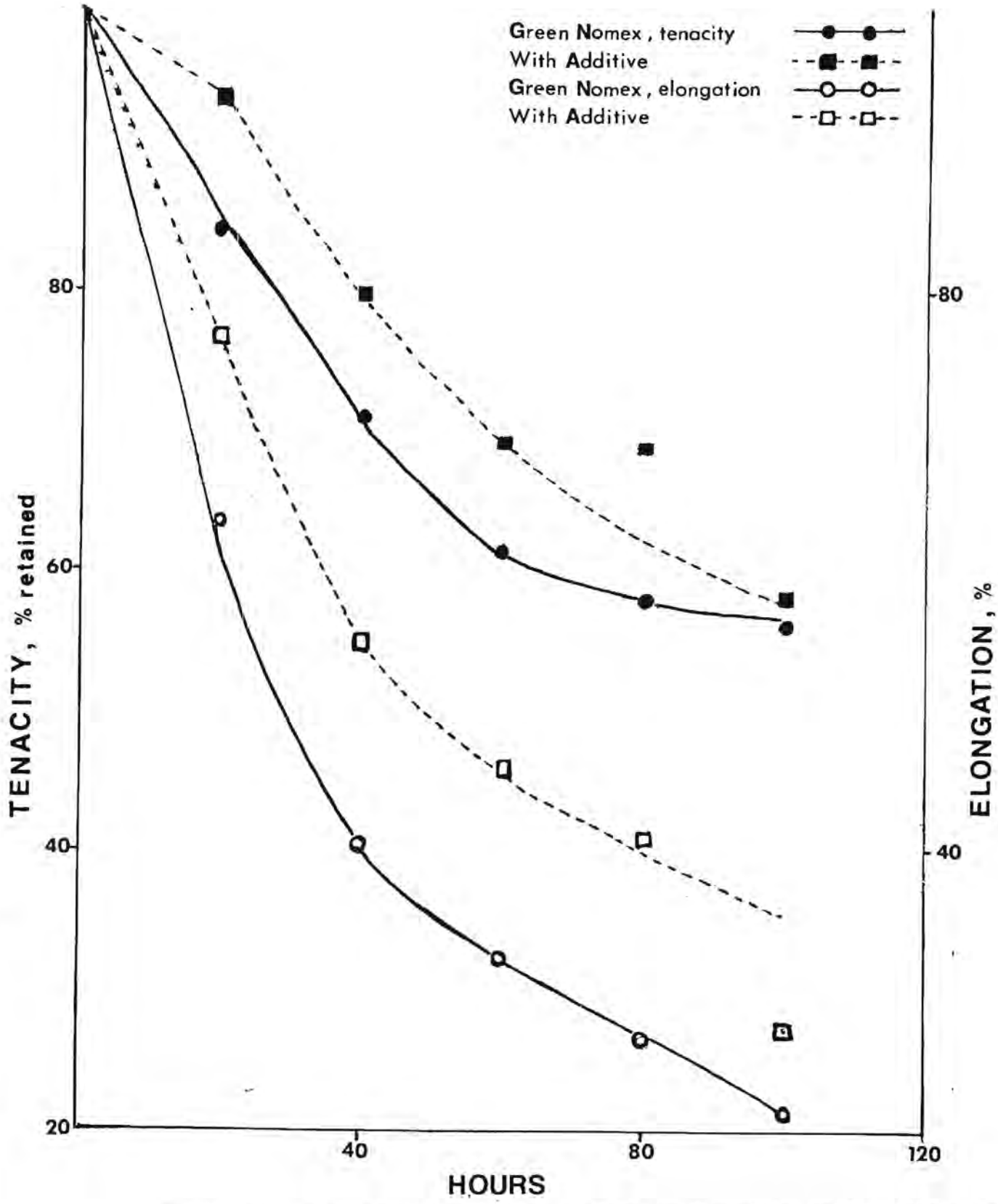


Figure 1 -- Retention of tenacity and elongation of Nomex Type 433 containing Blancophor AW compared to control sample after carbon-arc exposure.

as a stabilizer for Nomex. Retention of tenacity and elongation for Nomex (type 433) with and without Blancophor AW after exposure to up to 100 hours in the Carbon-arc Fade-O-Meter are shown in Figure 1. Improvement in retention of both tenacity and elongation was observed for the samples containing the additive. No other fluorescent brightener has shown similar effects on Nomex stability.

Although fluorescent brightening agents are strong absorbers in the near-UV region, they are not very stable to UV light. Loss of possible protection by degradation of the brighteners is therefore probably responsible for the inability of these materials to substantially improve the stability of Nomex. Recent discussions with a leading manufacturer of optical brighteners about possible addition of materials to stabilize the brighteners has indicated that they have attempted to do this in the past with little success.

A complete summary of the work on optical brighteners will be included in the January monthly report.

IV. Studies on Sulfur Containing Stabilizers

As noted in previous monthly reports, sulfur containing compounds and in particular sulfur dyes (containing disulfide bonds -S-S-) have been reported to stabilize aromatic polyamides against UV degradation. Two techniques for in-situ production of sulfur containing compounds were employed - reaction between urea and thiourea and acid decomposition of sodium thiosulfate.

The treatments of Nomex with aqueous solutions of urea and thiourea were as follows:

1. Urea 100g/l

2. Thiourea 100g/l

3. Urea and thiourea, 50g/l with respect to each

Skeins (2.5g) of Nomex yarn, Type 430, were treated in 125 ml of these solutions at 250°F for two (2) hours followed by rinsing to remove superficially held urea and thiourea. The treated yarns were then subjected to Fade-Ometer exposure.

An attempt was made to produce colloidal sulfur in Nomex by first treating the yarn in a solution of formic acid (40 g/l) at 250°F for 2 hrs. followed by a treatment with an aqueous solution of sodium thiosulfate (10 g/l) at 212°F for 15 minutes. It is known that this reaction produces colloidal sulfur. The treated yarns were then subjected to Fade-Ometer exposure.

Retention of tenacity and elongation on exposure to the Carbon-arc Fade-Ometer for samples containing urea are shown in Figure 2. The significant reduction in both properties by the presence of urea is obvious. Similar results for samples containing thiourea and urea plus thiourea are shown in Figures 3 and 4. In these cases almost no effect on properties is observed.

Results for samples containing colloidal sulfur are shown in Figure 5. No effects of the additive are noted in this case either. These findings suggest that compounds containing disulfide bonds are not stabilizers for Nomex and this approach will not be pursued further.

The observation that urea adversely affects the properties of Nomex exposed to UV radiation was an interesting and unexpected result. It may suggest that terminal $-NH_2$ groups in the polymer are involved in the digradation mechanisms. Techniques to remove terminal $-NH_2$ groups by

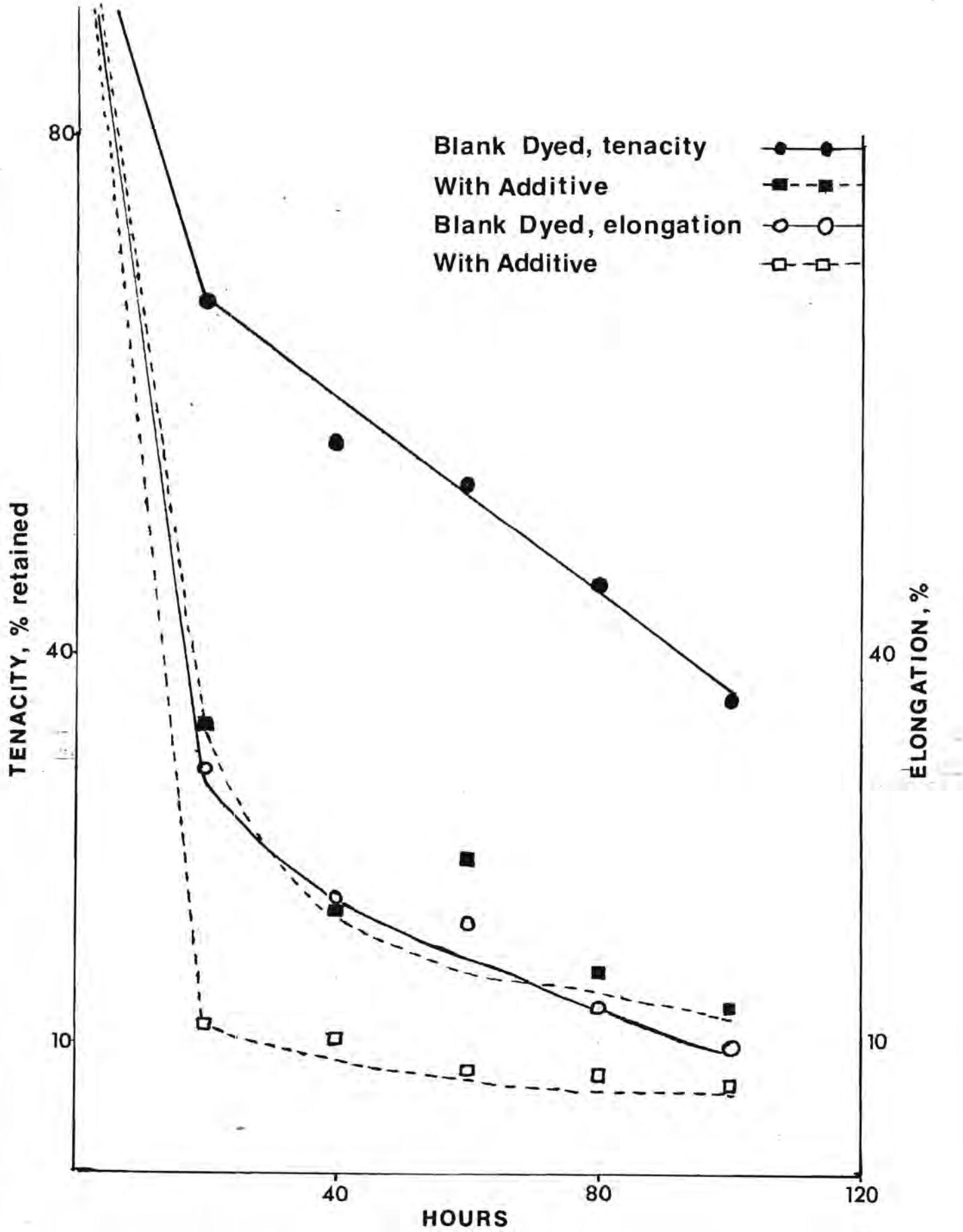


Figure 2 -- Retention of tenacity and elongation of Nomex Type 430 containing urea compared to control sample after Carbon-arc exposure.

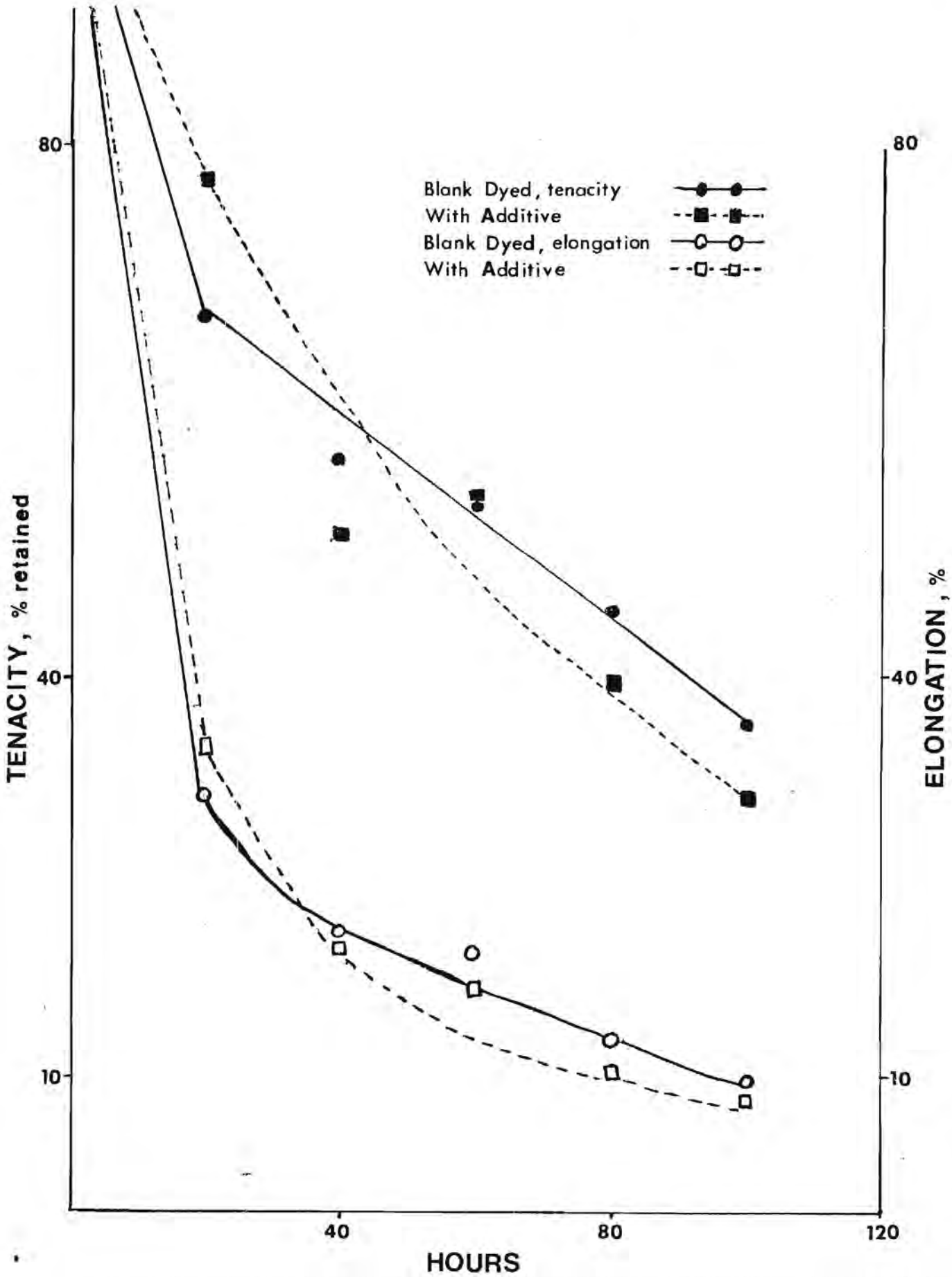


Figure 3 -- Retention of tenacity and elongation of Nomex Type 430 containing thiourea compared to control sample after Carbon-arc exposure.

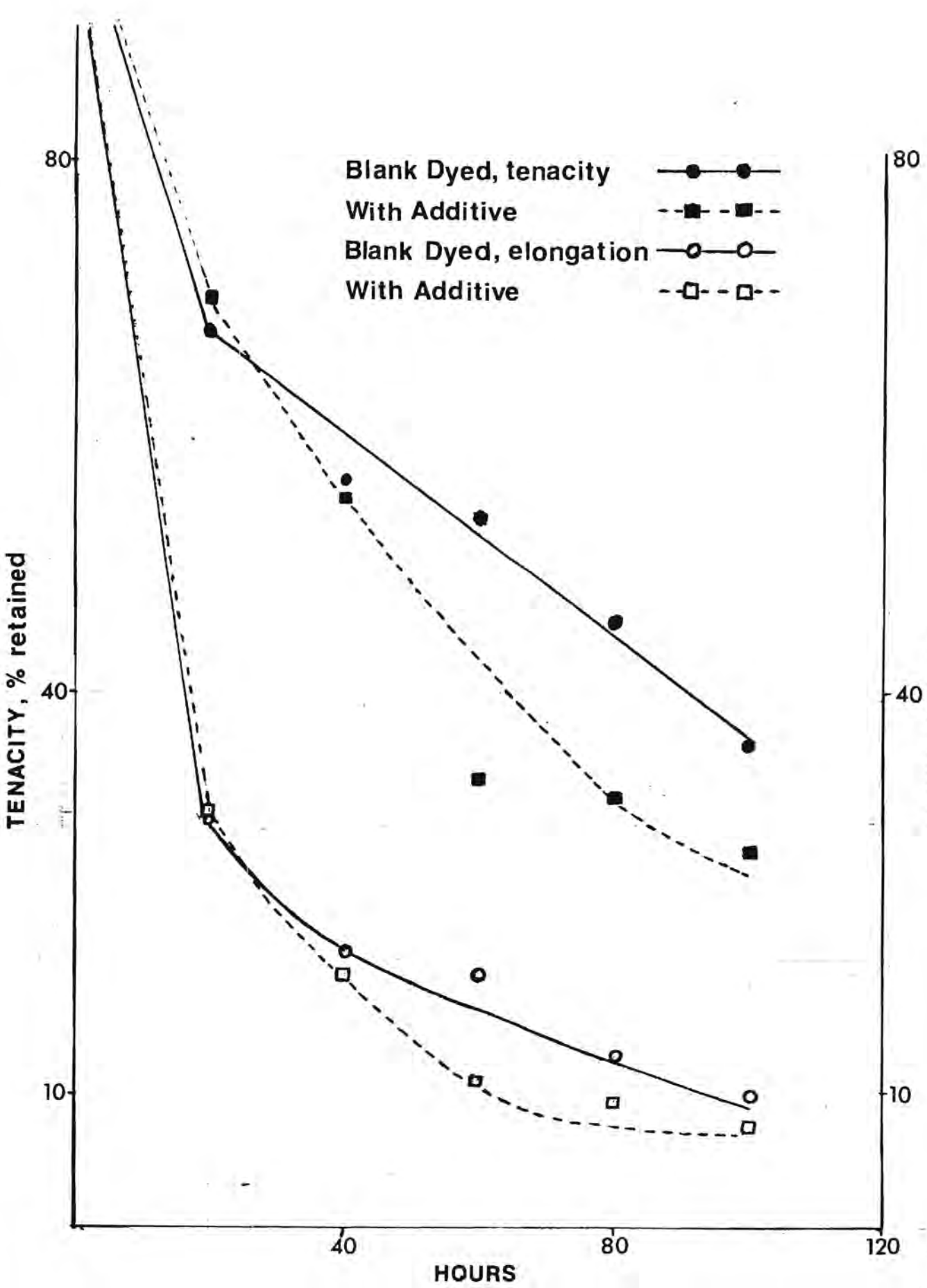


Figure 4 -- Retention of tenacity and elongation of Nomex Type 430 containing urea and thiourea compared to control sample after Carbon-arc exposure

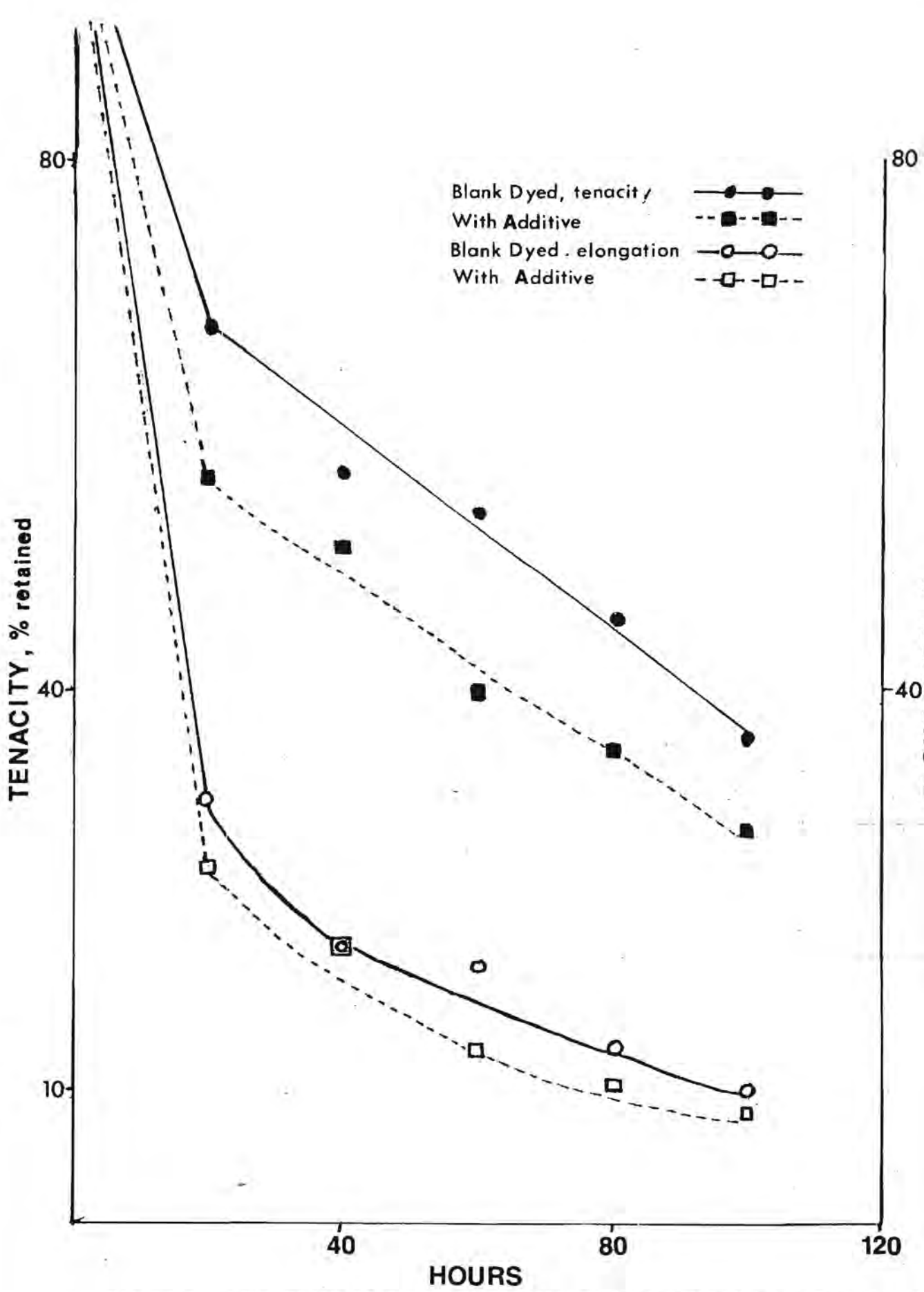


Figure 5 -- Retention of tenacity and elongation of Nomex Type 430 containing colloidal sulfur compared to control sample after Carbon-arc exposure.

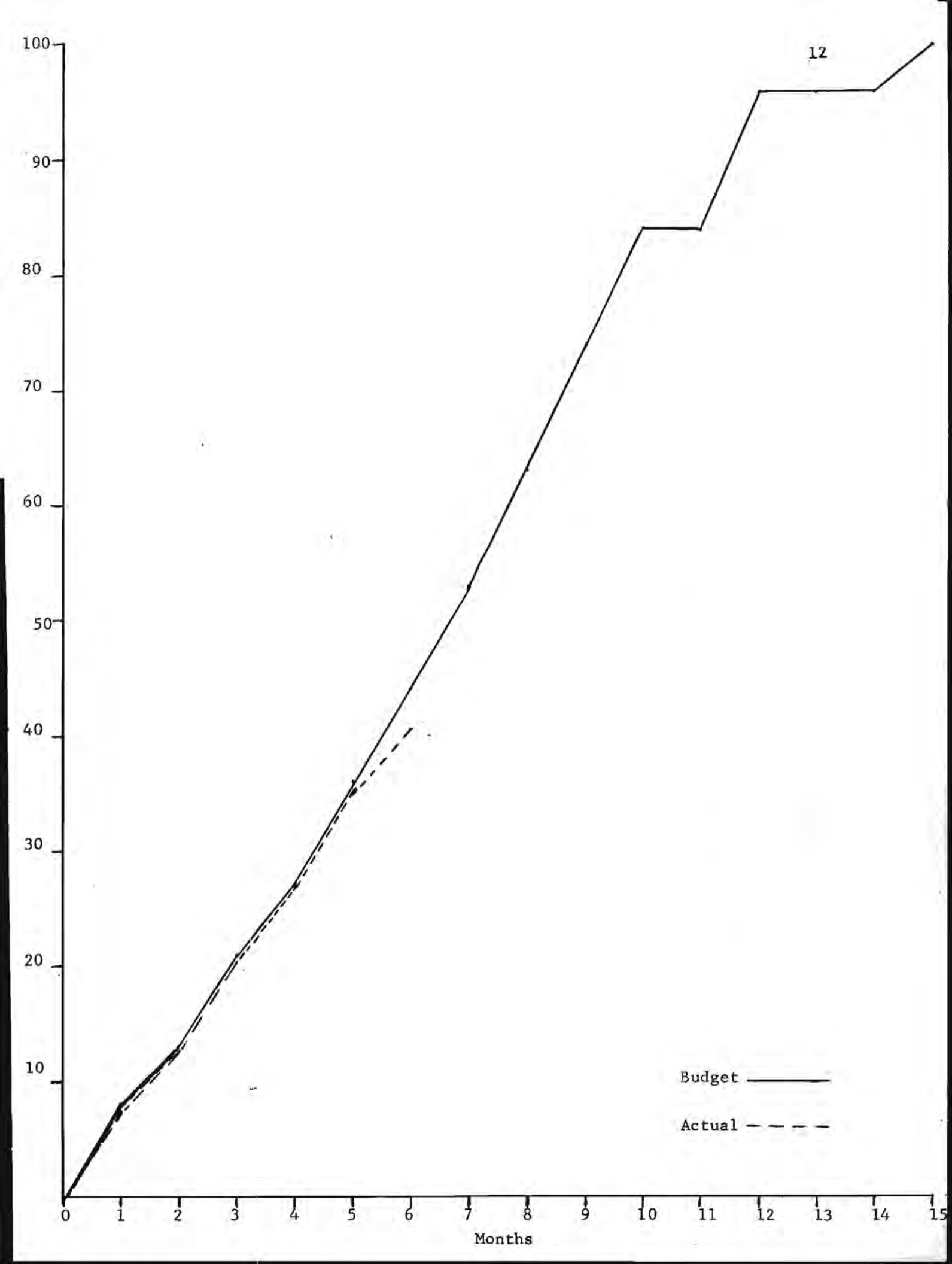
chemical reaction will be explored and the effect on light stability evaluated if a suitable technique can be found.

V. Future Work

Next month attention will be directed toward addition of UV screening agents of the benzotriazole type and metal atom containing excited state "quencher" stabilizers.

VI. Budget

The funds budgeted and either expended or allocated for the first six months are shown on the attached graph.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Months

VII. References

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2. Baird, B.R.; "Aromatic Polyamides Stabilized with Nickelous Carbonate"; U.S. Patent 3, 819, 569; June 1973.

3. Day, M. and Wiles, D.M.; "Effect of Light on the Flammability of Nomex Fabric"; Textile Research Journal, 44, 888 (1974).

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E-27-623

Monthly Progress Report Number 7

(Dec. 26, 1974 - Jan. 26, 1974)

Development of Ultraviolet Protection Nomex

Life Support SPO
Air Force Systems Command
Aeronautical Systems Division
Wright-Patterson Air Force Base, Ohio 45433

(Prepared Under Contract No. F33657-74-C-0716
by
Georgia Institute of Technology
Atlanta, Georgia 30332
W. C. Tincher, author)

SUMMARY

A number of ultraviolet screening agents have been tested for reduction of Nomex UV degradation. These materials act as stabilizers by competing with the fiber for the UV light responsible for degradation. Of the materials tested two, Blancophor AW and Tinuvin P, show promise for improving the light stability of Nomex. Since the UV screening agent phase of the project is essentially complete, a review of that part of the project is included in this monthly progress report.

Experiments are nearing completion on stabizers which act by quenching excited states involved in Nomex UV degradation.

The second review meeting with Air Force personnel is scheduled for February 5 at the Georgia Institute of Technology.

TABLE OF CONTENTS

I. Introduction

Studies are essentially complete on ultraviolet screening agents for improvement in Nomex UV degradation. A complete review of this phase of the work has therefore been included in this monthly progress report.

II. Selection of UV Screening Agents

UV screening agents improve the light stability of fibers and fabrics by competing with the substrate for photons responsible for degradation. To be effective, screening agents must have two important characteristics. First, they must have strong absorption in the same region of electromagnetic radiation as the substrate. Second, the screening agent must have means of dissipating the excess energy obtained by absorption of electromagnetic radiation without degrading itself or stimulating the degradation of the substrate. These are rather stringent requirements and only a few chemical structures can function as UV screening agents.

The absorption spectrum of Nomex in the near UV and visible region which is responsible for Nomex photodegradation is shown in Figure 1. Compared to most fiber-forming polymers the absorption of Nomex is much nearer the visible region of the spectrum. Sunlight has a significant quantity of energy in this region which may account for the sensitivity of Nomex to UV degradation. Unfortunately, most UV screening agents designed for improving stability of polymeric materials absorb strongly further in the UV than Nomex. The overlap between screener absorption bands and the Nomex degradation band is not as large as desirable for maximum efficiency.

One class of materials which do have strong absorption bands in the same region of the spectrum as Nomex is the fluorescent brightening agents. An absorption spectrum for a typical brightener is shown in Figure 2. A comparison of Figure 2 and Figure 1 indicates that fluorescent brighteners should be able to compete effectively with Nomex for the photons responsible for degradation. In addition, the brightening agents can lose excess energy by fluorescence and will therefore show sufficient stability to be of interest as UV screening agents.

Five optical brighteners were selected for investigation. Data on these materials are given in TABLE 1. All are optical brighteners recommended for use on polyamides and are reported to be among the more stable optical brighteners to UV degradation.

In addition to the optical brighteners investigated, studies were also conducted using conventional UV screening agents (absorbers). Because of their excellent performance in a wide range of polymers and reports in the literature on their stabilizing effects in Nomex, the Tinuvin series of screening agents was selected for study. The Tinuvins are substituted hydroxyphenyl benzotriazoles which have strong absorption in the near UV and have excellent stability to UV degradation. Tinuvin P and Tinuvin 327 were the specific compounds used in this investigation.

In addition one substituted Triazine type UV absorber, Cyasorb UV-800 (American Cyanamid) was also included in the study.

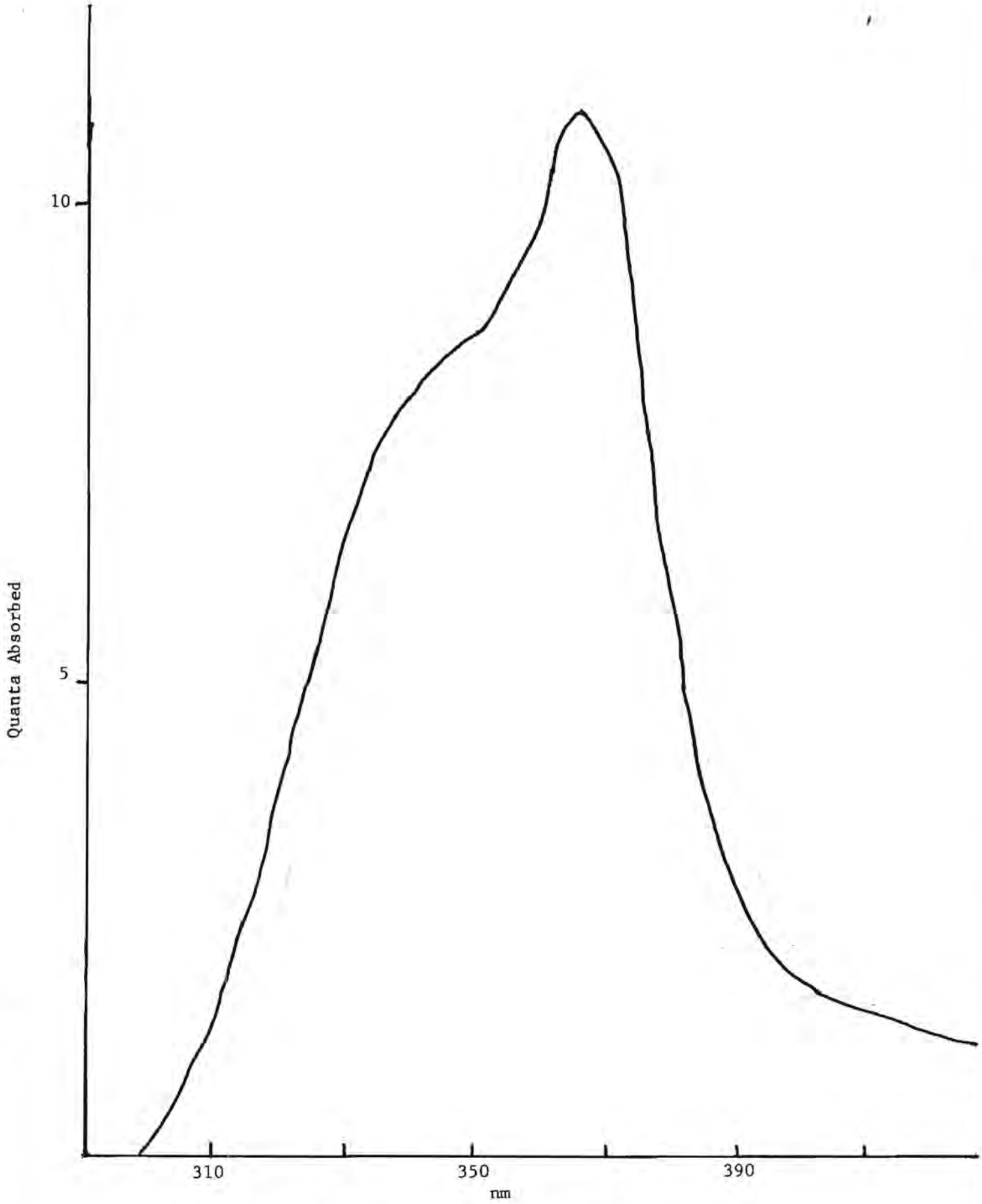


Figure 1 - Absorption Spectrum of Nomex

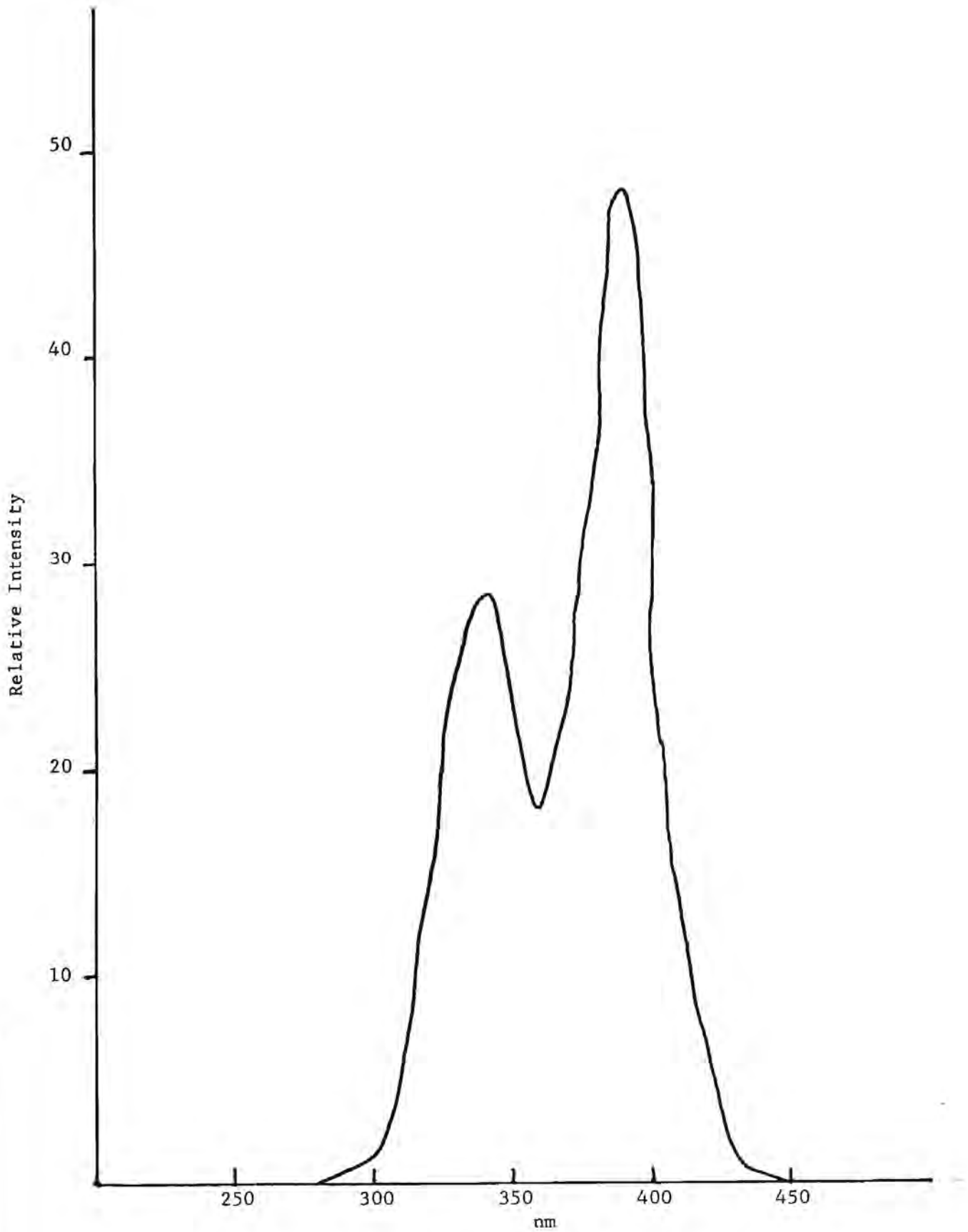


Figure 2 - Absorption Spectrum of Uvitex RBNAD

TABLE 1

Optical Brighteners Selected as Candidates

For Nomex Stabilization

Name	C.I. Number	Manufacturer	Structure
Uvitex WGS	FB-56	Ciba-Geigy	Coumarine Derivative
Blancophor AW	F8-61	GAF	- -
Uvitex RBNAD	FB-59	Ciba-Geigy	Stilbene Derivative
Leucophor EFR	FB-162	Sandoz	- -
Uvitex NFW	-	Ciba-Geigy	- -

III. Addition of Screening Agents to Nomex

Screening agents were applied to Nomex Type 433-Sage Green 200 denier, 100 filament yarn samples by procedures similar to those used for dyeing of Nomex fiber. The fiber (2.5 grams) was wound loosely on a stainless steel wire flame and placed in stainless steel cans containing the treatment solution. Composition of the treatment bath was

2.5 grams optical brightener or UV absorber

5.0 ml Chemocarrier FRN (Tanatex)

125 ml total volume of bath (50:1 liquor ratio)

The cans were sealed and placed in an Atlas High Temperature Launder-Ometer at room temperature. The temperature was raised to the treatment temperature (250°F for optical brighteners and 260°F for the UV absorbers) at 3°F per minute. The temperature was held at 250°F (or 260°F) for two hours followed by a 15 minute cooling cycle. The fiber samples were then removed and scoured in a bath containing

5.0% Merpol HC (o.w.f.)

6.0% $Na_4 P_2 O_7 - 3 H_2O$ (o.w.f.)

125 ml total volume of scouring bath (50:1 liquor ratio)

The scouring was carried out at 180°F for 15 minutes followed by a thorough rinse.

A control sample (blank dyed sample) was prepared using the same procedure described above except that the optical brigthener and UV absorber were omitted.

For these preliminary screening studies, no attempt was made to obtain quantitative data on the quantity of optical brighteners or UV absorber actually picked-up from the bath by the Nomex fiber. Fibers were examined under a UV light following the treatment with optical brighteners and it was apparent that substantial quantities of the brighteners had been incorporated in the fiber.

IV. Exposure and Testing

Control samples, samples which had been blank dyed and samples containing UV screening agents were exposed to light from either a xenon-arc or carbon-arc in Atlas Fade-Ometers. Xenon-arc exposures were carried out in a Model F Fade-Ometer equipped with a preaged 2500 watt arc with IR absorbing inner and quartz outer filters. The Fade-Ometer is equipped with a humidity control unit and was operated at a black panel temperature of 150°F and a relative humidity of 50%. Samples were exposed up to 100 hours with specimens removed from the Fade-Ometer at 20 hour intervals.

Carbon-arc exposures were conducted in a Type W Weather-Ometer with twin enclosed carbon-arcs. Relative humidity was maintained at 50% and the black panel temperature at 150°F.

In each series of exposures, both control and "blank-dyed" samples were exposed simultaneously with the treated specimens.

Breaking strength and elongation of yarns were tested with an Instron constant-rate-of-extension tester, following procedures described in ASTM method D 2256. Tests on control and irradiated yarns were made with a 5 inch

gage length and an extension rate of 100 percent per minute. The time required to break is a function of gage length, extension rate, and breaking elongation. Since breaking elongation was expected to vary with level of irradiation, time-to-break was not used as a criterion of testing as specified in the ASTM method. The 5-inch gage length was chosen to accommodate the relatively short yarn lengths exposed to the UV light source.

Because of the difficulty of securing the same tension in all the filaments and because of slippage in the clamps, erratic results are frequently obtained with zero-twist multifilament yarns unless a small amount of twist is inserted before testing. A twist of $(110 \pm 10 \text{ tpi})/\sqrt{D}$, where D is the multifilament yarn denier, was used to overcome these problems.

Twenty tests were made on each sample. This level of testing was selected to provide a maximum error of ± 3 percent for strength and ± 5 percent for elongation of the control yarns. Variation in observed results of both of these properties were expected to increase with increased levels of irradiation Consequently, the error in estimation of these properties measured on the exposed yarns can be expected to be somewhat higher.

V. Results and Discussion

The percent retention of tenacity and elongation of Nomex Type 430 yarn samples exposed to the xenon- and carbon-arc are shown in Figures 3 and 4. It is obvious from these experiments that carbon-arc exposure represents a much more severe test of UV stability. This is due to the very high output

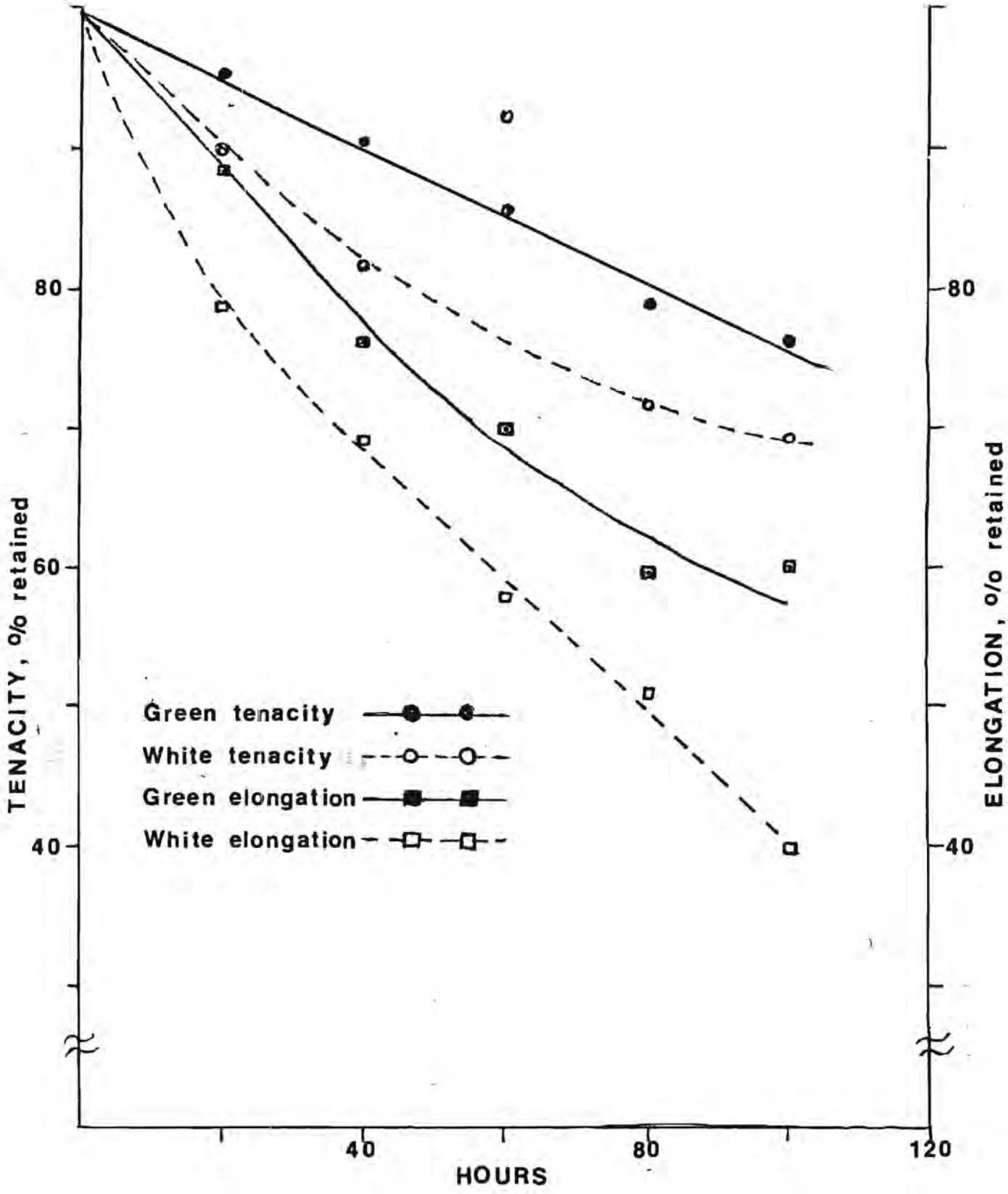


Figure 3. Retention of tenacity and elongation of Nomex Type 430 (white) and Type 433 (sage green) after Xenon-arc exposure

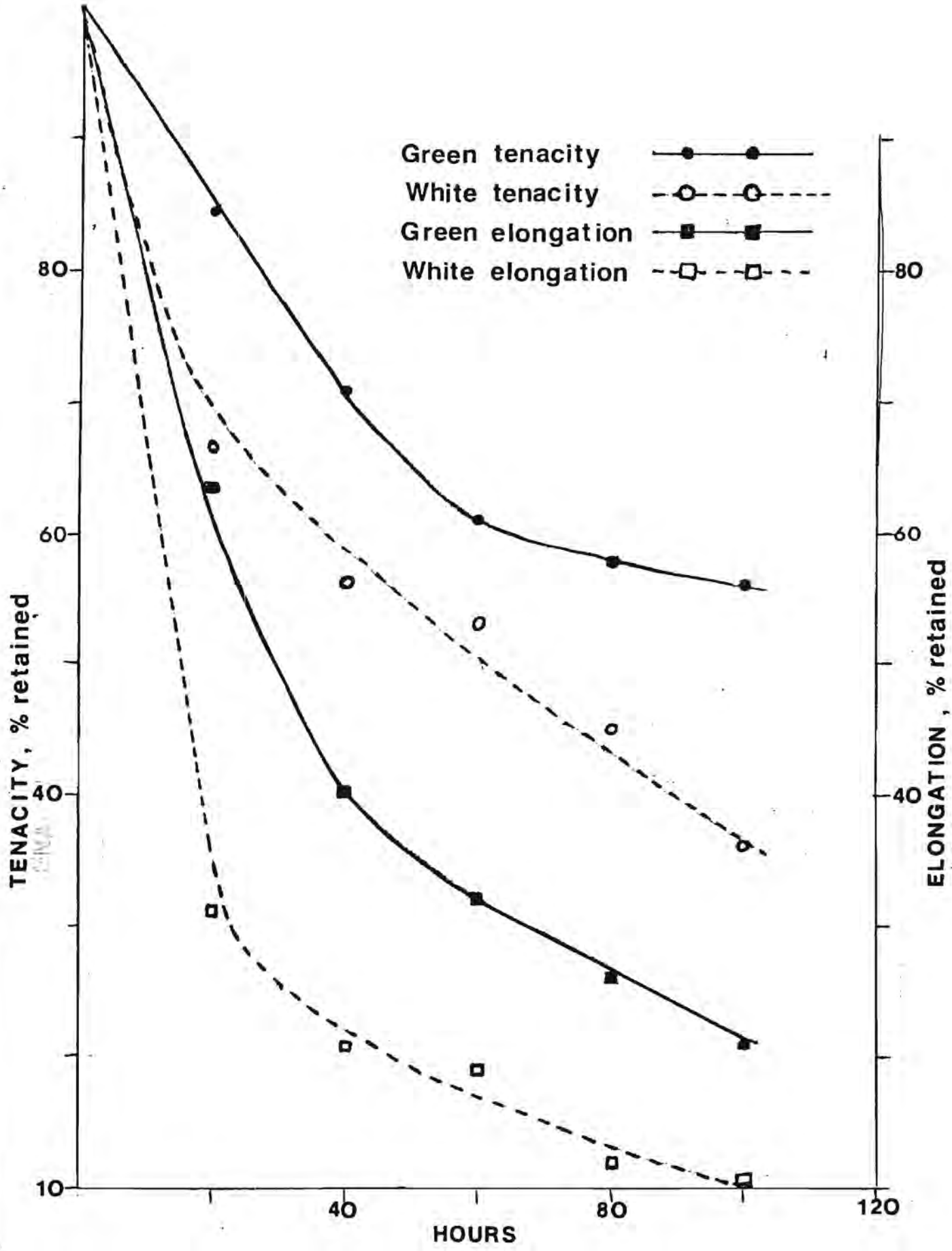


Figure 4. Retention of tenacity and elongation of Nomex Type 430 (white) and Type 433 (sage green) after Carbon-arc exposure

of the carbon-arc in the region of the UV spectrum responsible for Nomex degradation.

The effects of the "blank dyeing" on properties is illustrated in Figure 5. Some slight improvement in retention of elongation and in some cases retention of tenacity are observed from the "blank dyeing" alone. This is undoubtedly due to retention of small quantities of residual swelling agent (carrier) in the fiber which acts as a plasticizer in reducing the brittleness resulting from UV degradation. In a few cases, some loss in tenacity is observed for "blank dyed" samples. This probably results from mechanical damage to the yarn during the dyeing operations.

A. Samples Containing Optical Brighteners

The retention of tenacity and elongation of Nomex yarns containing optical brighteners after 0, 20, 40, 60, 80, and 100 hours exposure to the carbon-arc compared to similar exposures of blank dyed samples are shown in Figures 6 to 10. Similar data for xenon-arc exposure are shown in Figures 11 to 14.

Nomex yarn containing Leucophor EFR showed a significant reduction in both tenacity and elongation in all exposure experiments (Figures 6 and 11). This material is clearly capable of phototendering Nomex. Samples containing Uvitex WGS (Figures 7 and 12) indicate that this optical brightener has little or no effect on property retention on UV exposure. A similar conclusion is indicated by results on samples containing Uvitex RBNAD (Figure 8 and 13). Results are less clear for Uvitex NFW containing samples

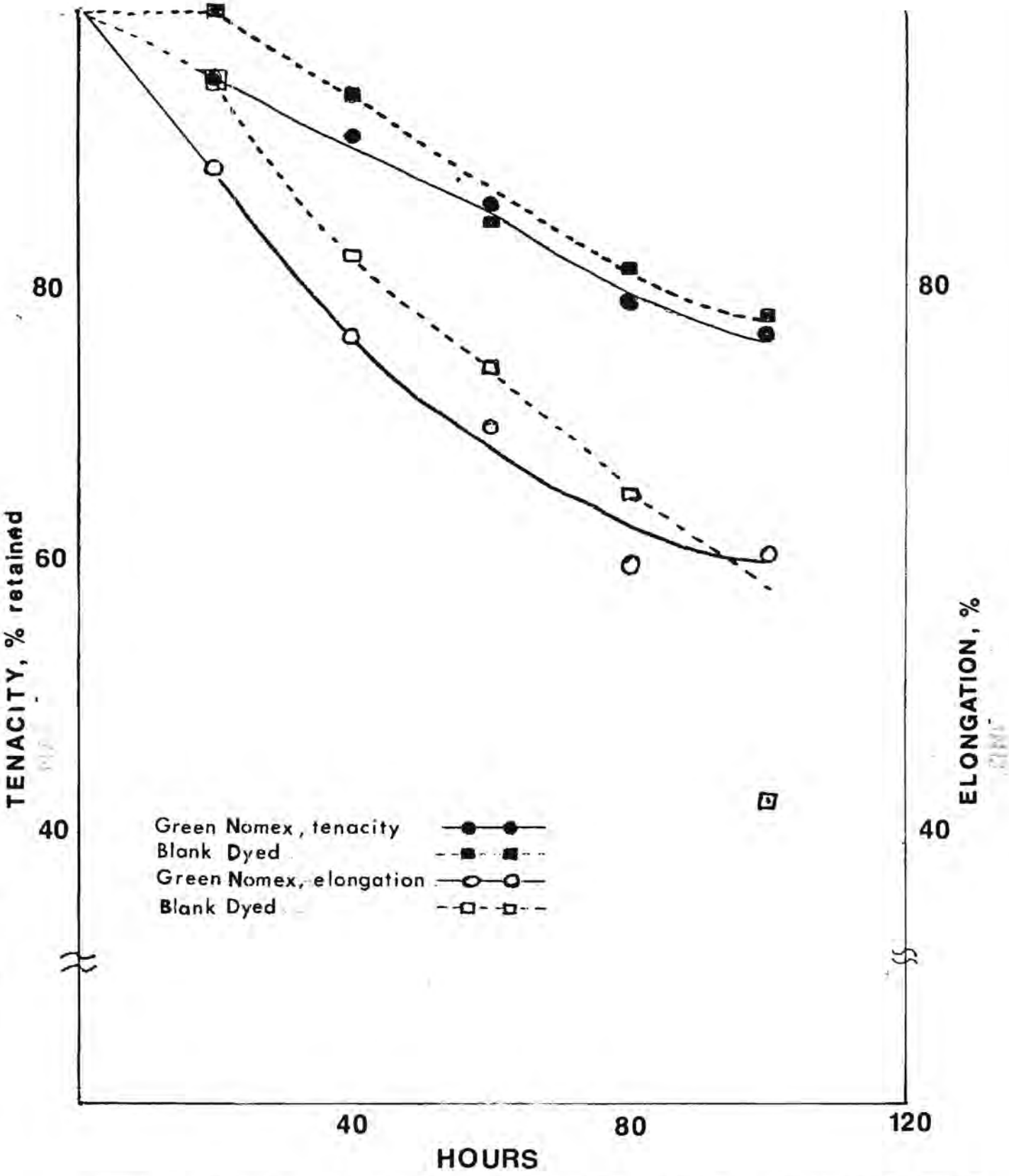


Figure 5. Retention of tenacity and elongation of Nomex Type 433 (sage green), control and blank dyed after xenon-arc exposure.

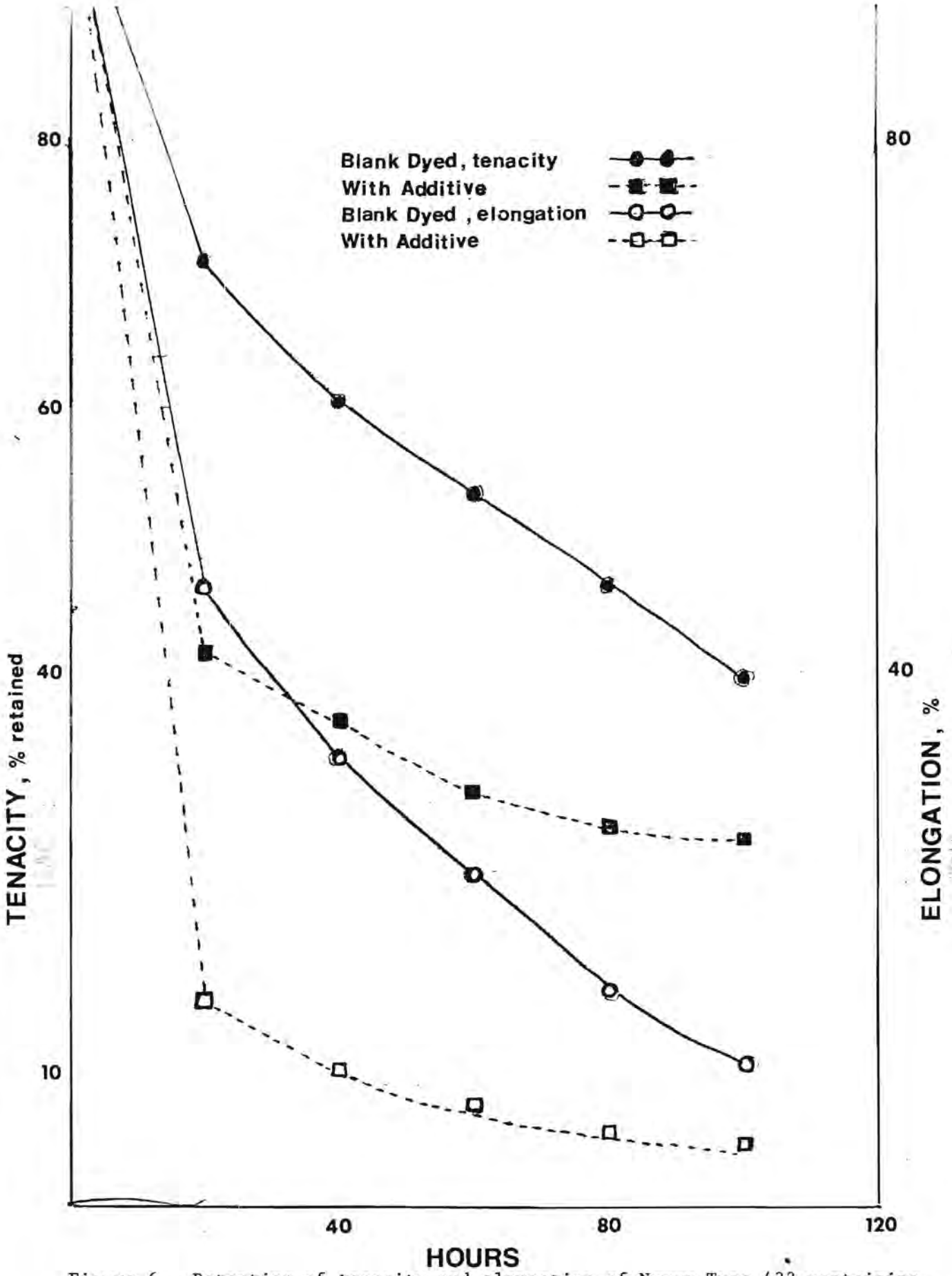


Figure 6. Retention of tenacity and elongation of Nomex Type 433 containing Leucophor EFR compared to control after carbon-arc exposure.

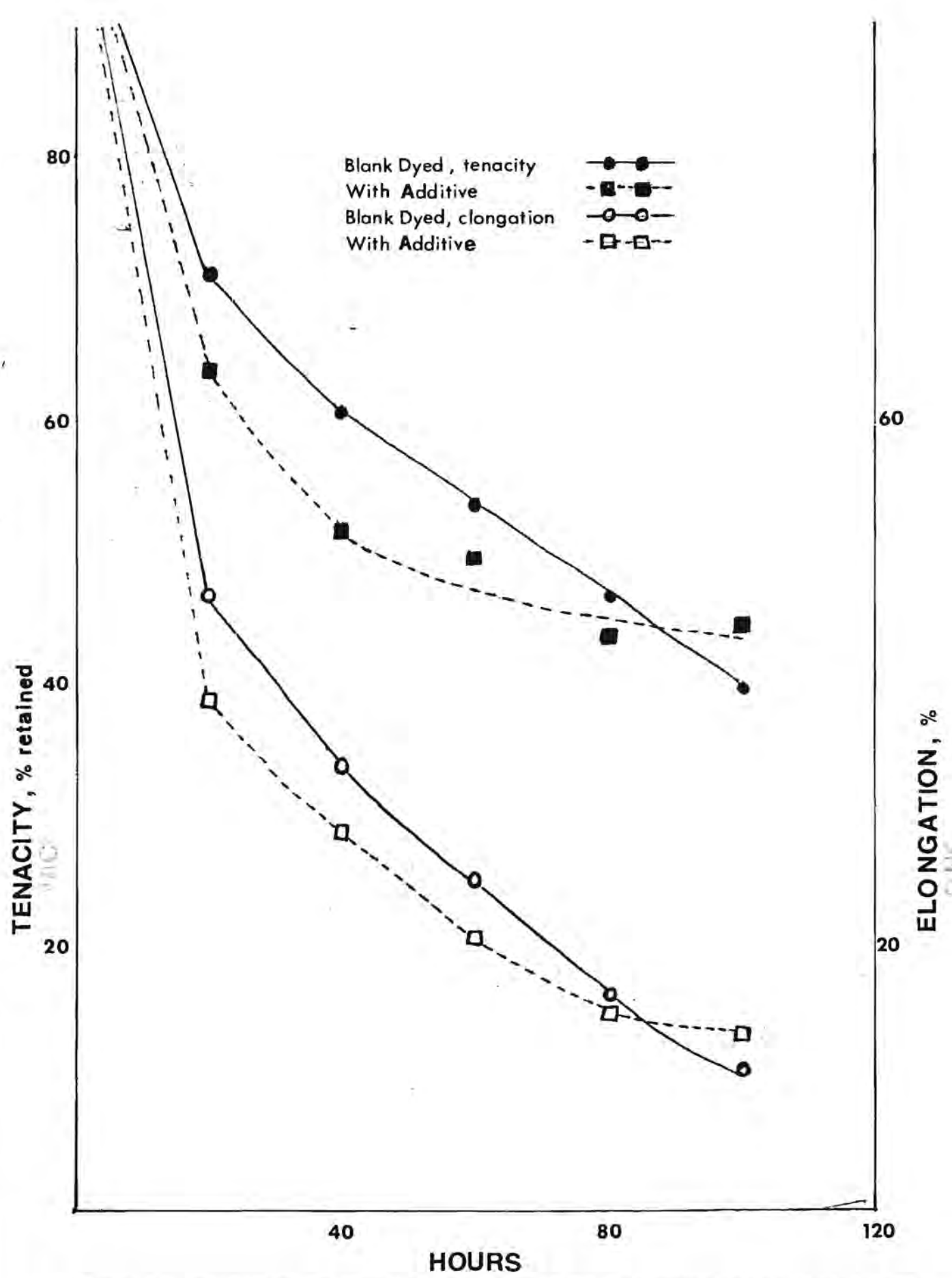


Figure 7. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex WGS compared to control after carbon-arc exposure.

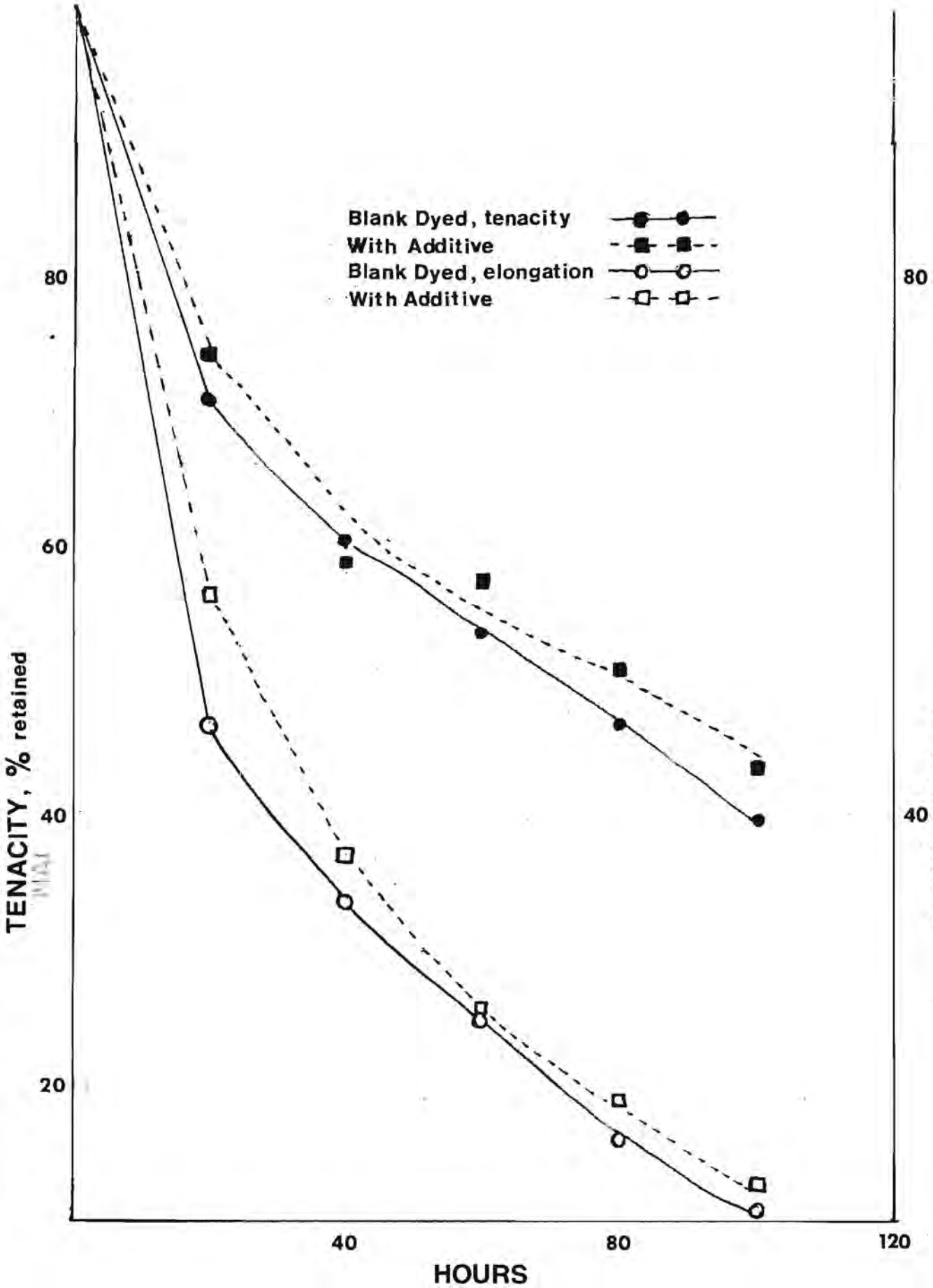


Figure 8. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex RBNAD compared to control after carbon-arc exposure.

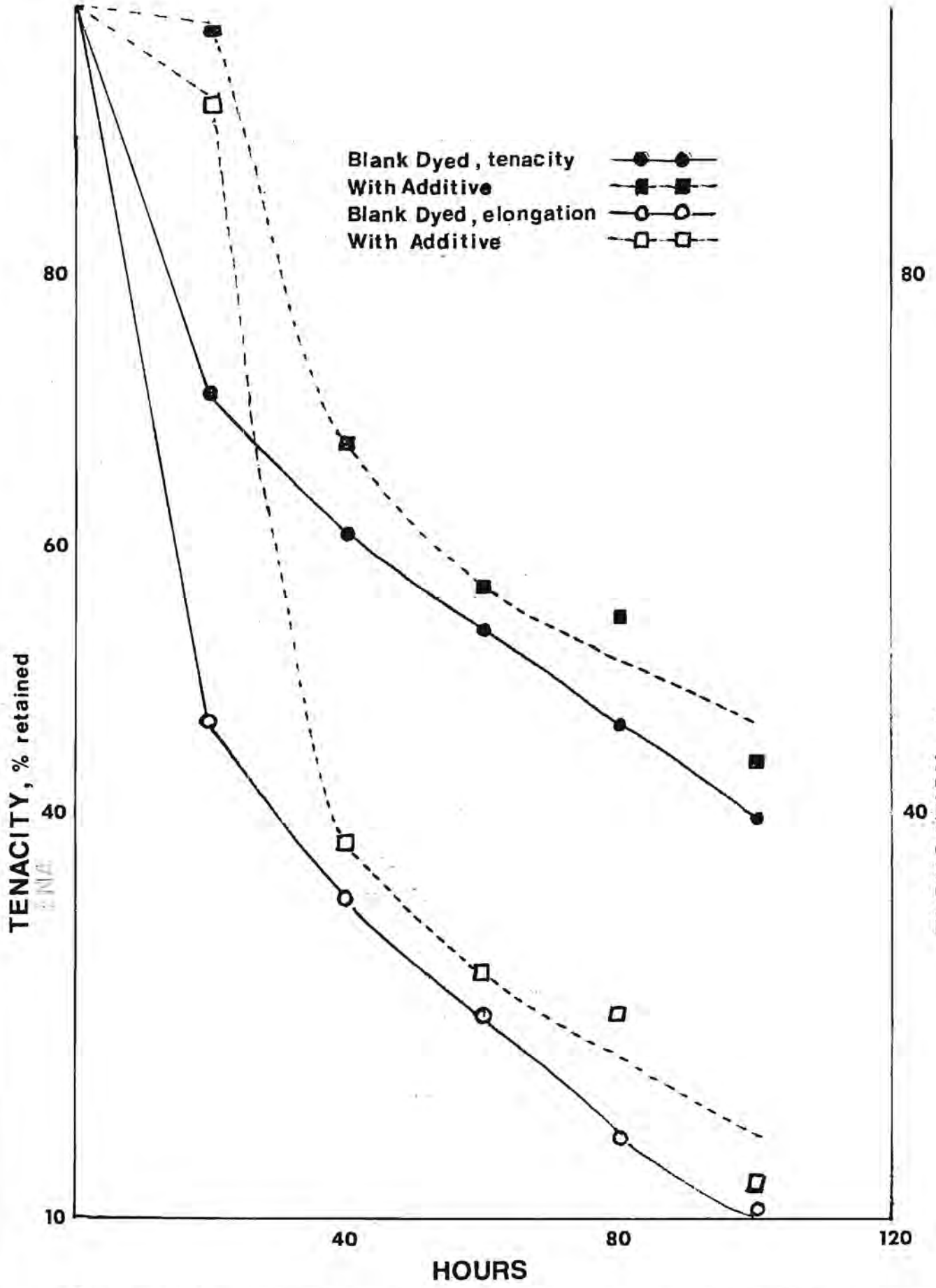


Figure 9. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex NFW compared to control after carbon-arc exposure.

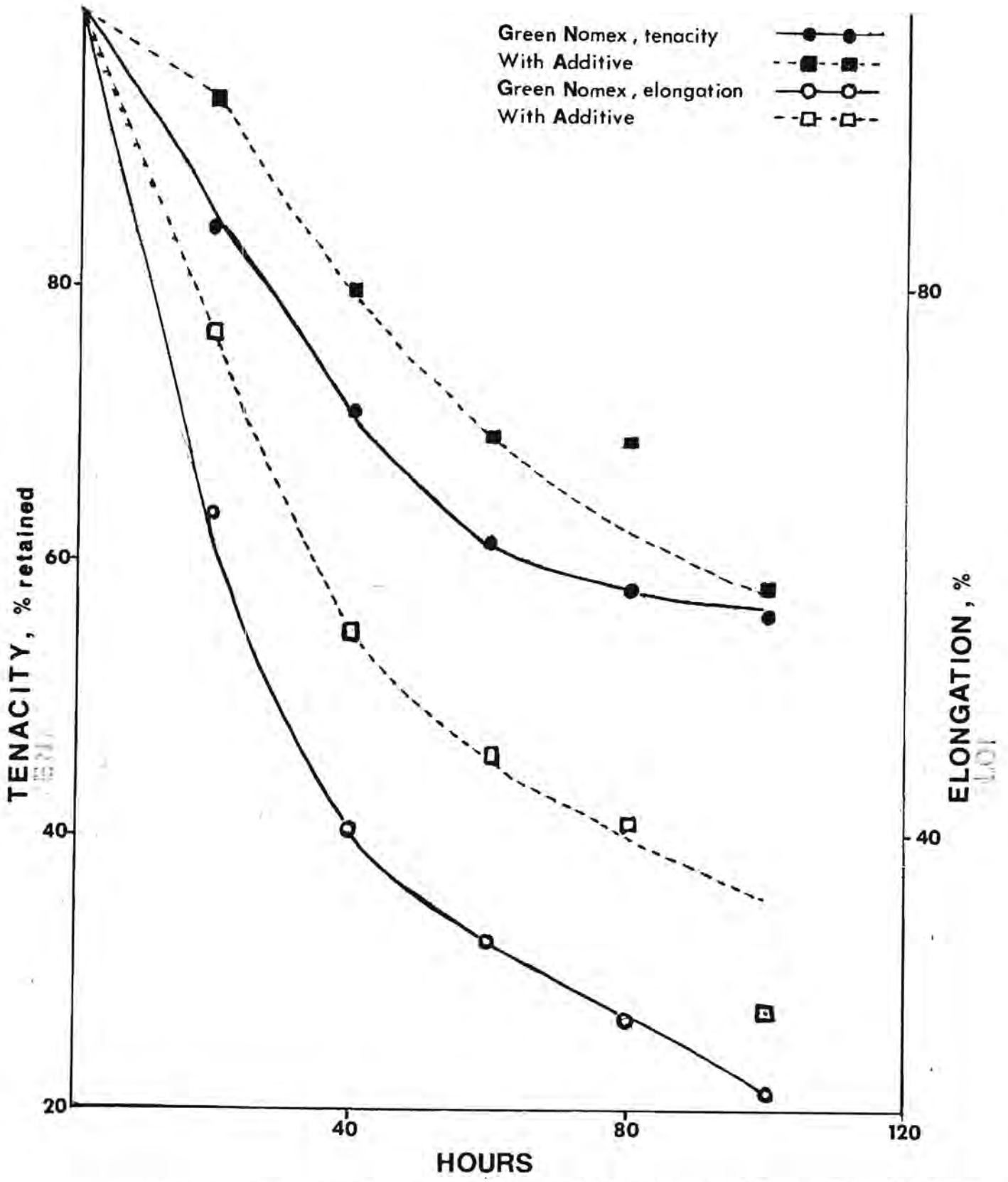


Figure 10. - Retention of tenacity and elongation of Nomex Type 433 containing Blancophor AW compared to control sample after carbon-arc exposure.

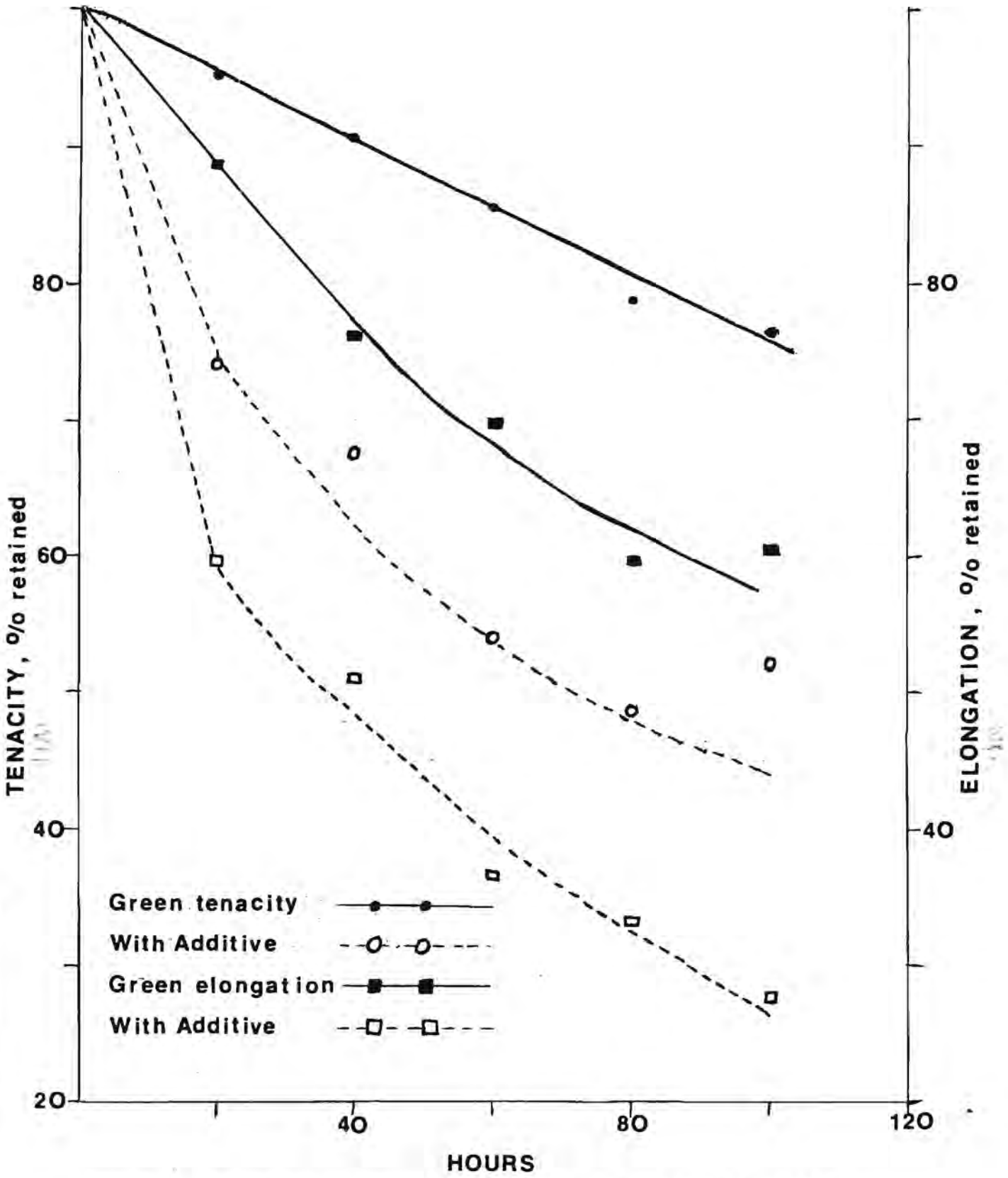


Figure 11. Retention of tenacity and elongation of Nomex Type 433 containing Leucophor EFR compared to control sample after Xenon-arc exposure

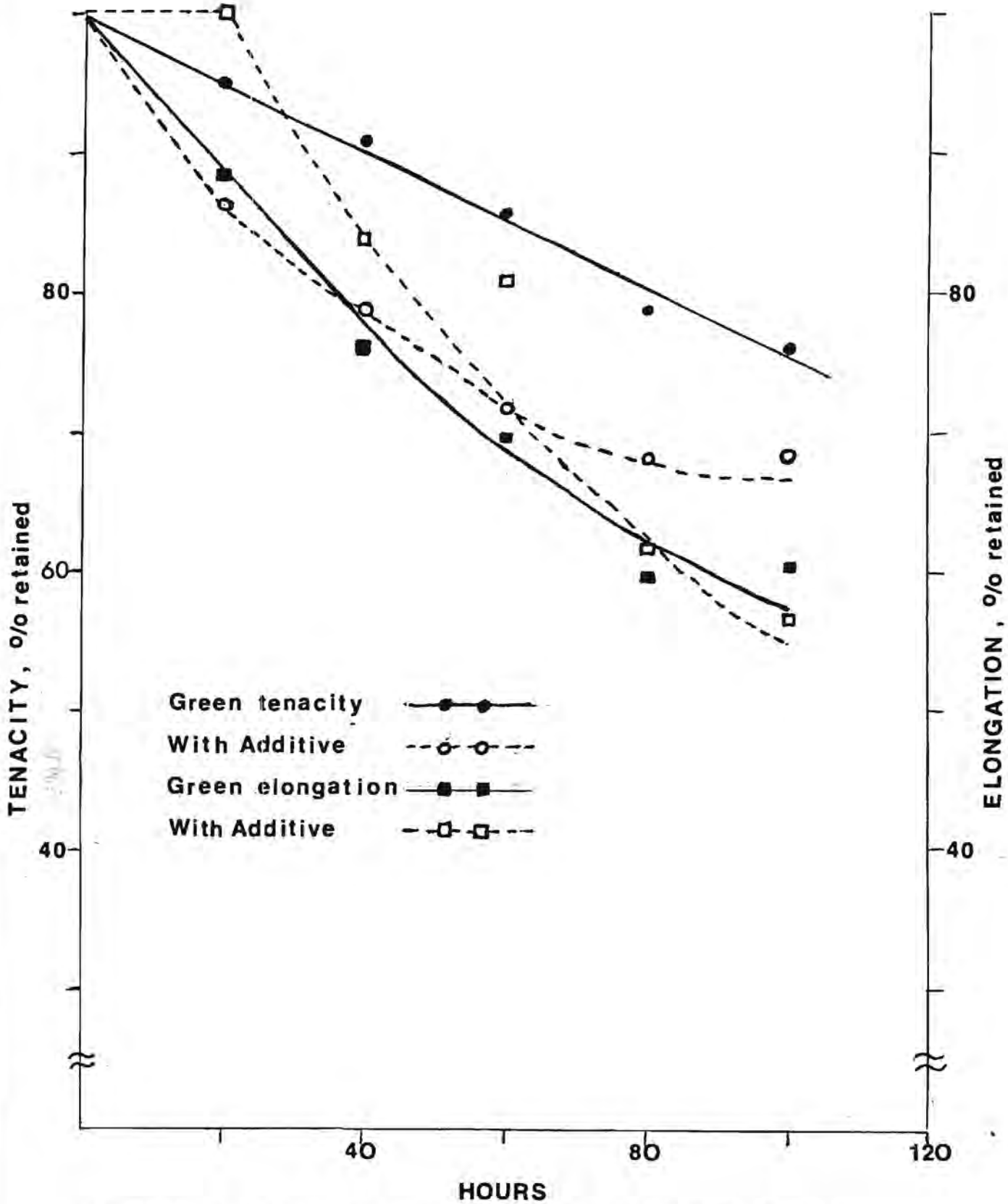


Figure 12. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex WGS compared to control sample after Xenon-arc exposure.

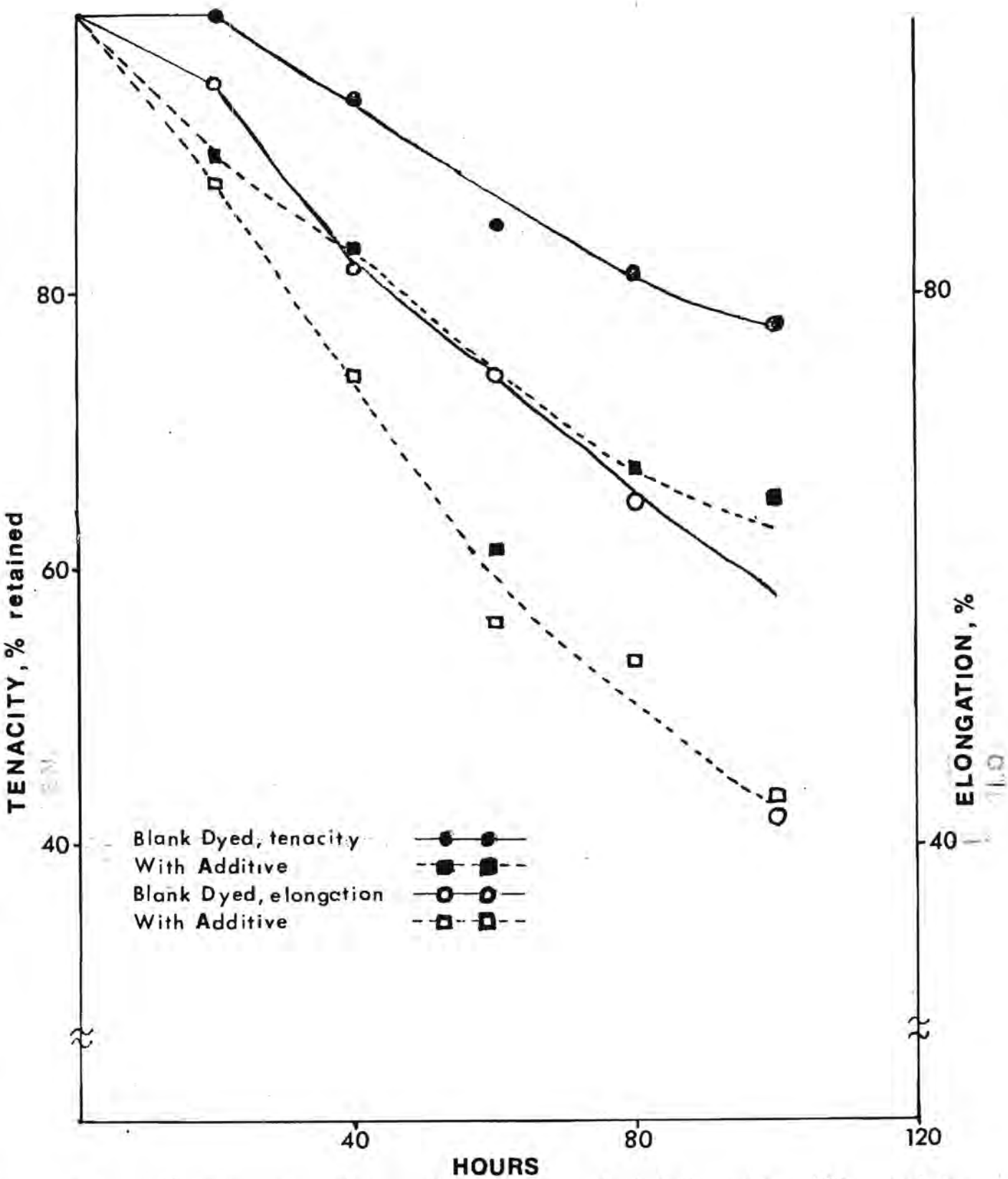


Figure 13. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex RBNAD compared to control after xenon-arc exposure.

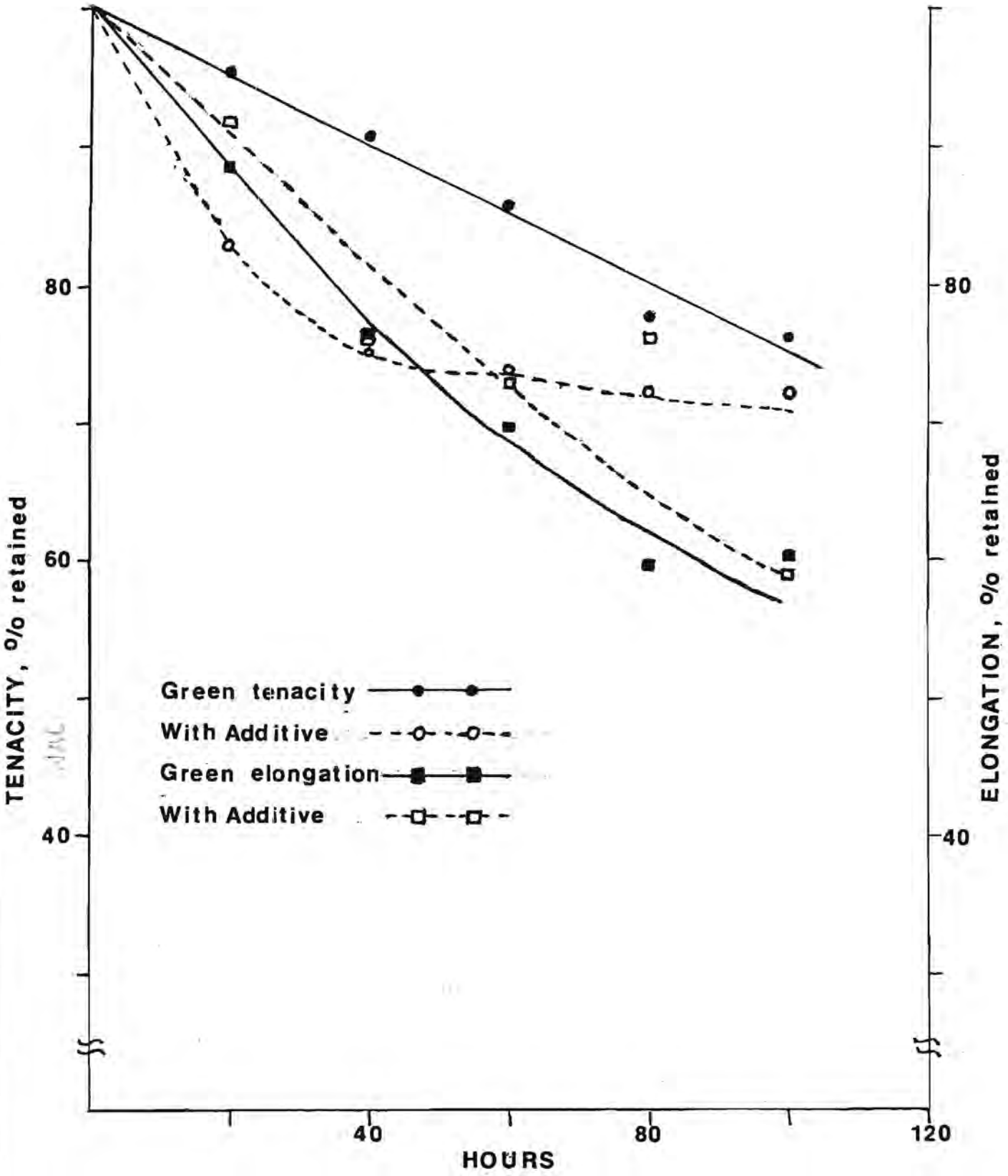


Figure 14. Retention of tensity and elongation of Nomex Type 433 containing Uvitex NFW compared to control sample after Xenon-arc exposure

(Figure 9 and 14). This brightener appears to have some protective effect in the first 20 hours of carbon-arc exposure. The stabilizing effect is rapidly lost however, probably due to degradation of the optical brightener itself. A similar stabilization is not observed for xenon-arc exposure. The higher UV output of the xenon-arc in the UV region may give a more rapid degradation of the Uvitex NFW. It should be noted results for xenon exposure of the Uvitex NFW containing sample appear to be somewhat erratic. It does, however, apparently provide some small stabilizing effect on Nomex degradation.

The most promising of the optical brighteners for Nomex stabilization appears to be Blancophor AW (Figure 10). This material gave a clear stabilizing effect at all exposure times. A statistical analysis of the data confirmed that Blancophor AW containing Nomex has significantly greater retention of tenacity and elongation than the blank dyed sample. Blancophor AW was therefore selected for further study.

B. UV Absorbers

The retention of tenacity and elongation of Nomex samples containing Tinuvin P is shown in Figure 15. These data clearly indicate that a stabilizing effect is observed at all exposure times. Similar results for Tinuvin 327 are shown in Figure 16. In this case the UV absorber apparently had an adverse effect on Nomex properties on exposure to the carbon-arc. Results for Nomex samples containing UV 800 are given in Figure 17. This

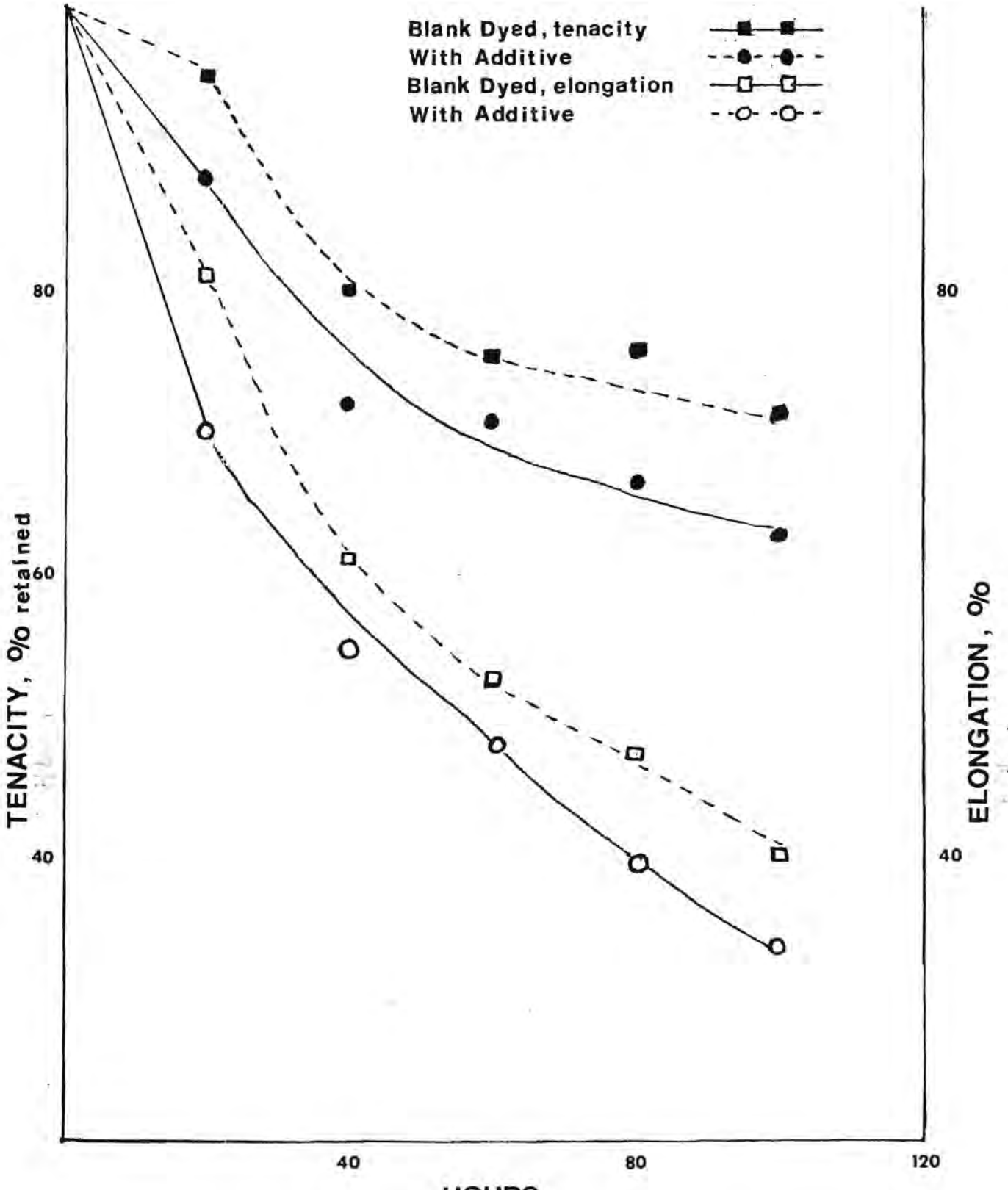


Figure 15. Retention of tenacity and elongation of Nomex Type 433 containing Tinuvin P compared to control after carbon-arc exposure.

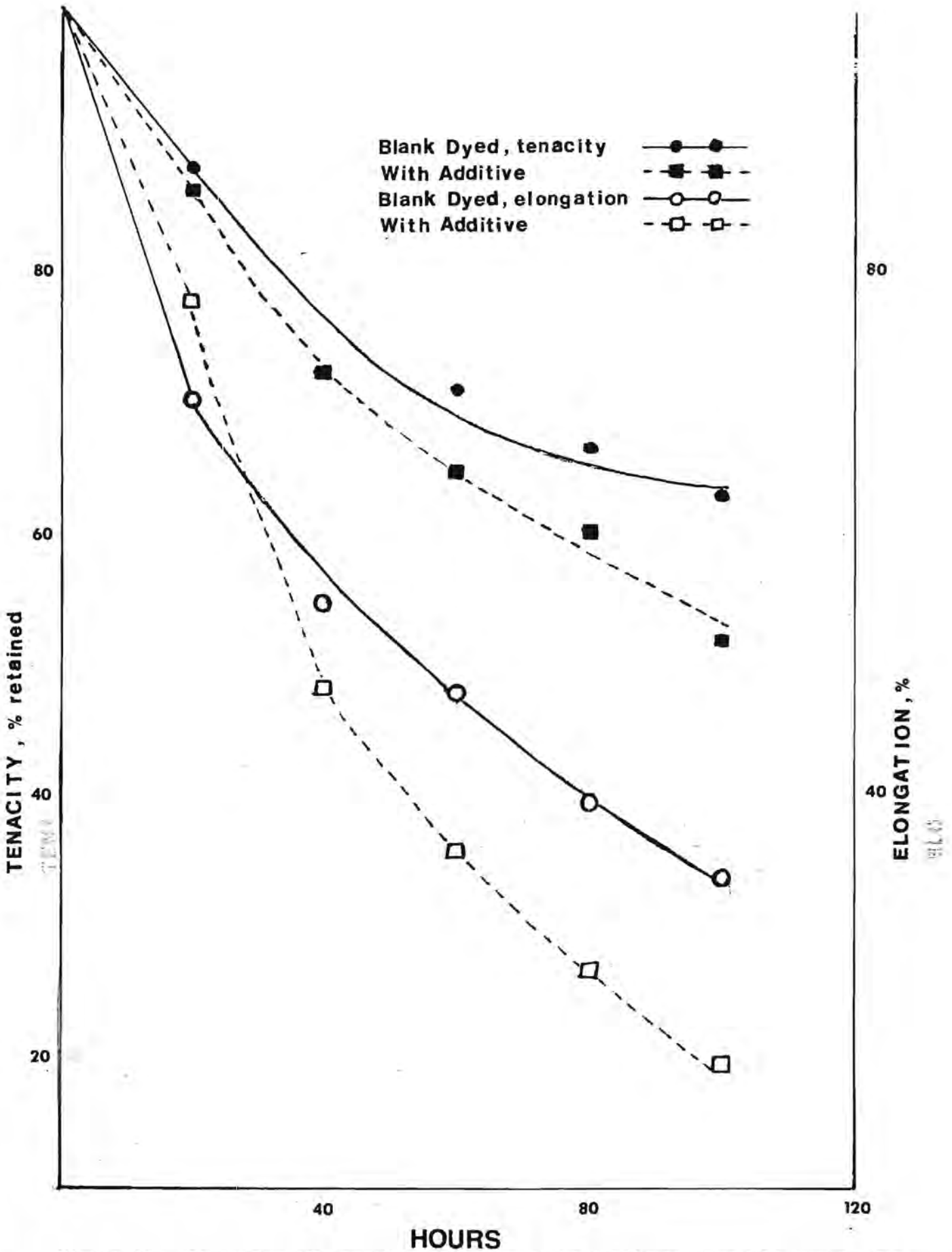


Figure 16. Retention of tenacity and elongation of Nomex Type 433 containing Tinuvin 327 compared to control after carbon-arc exposure.

TINUVIN 327

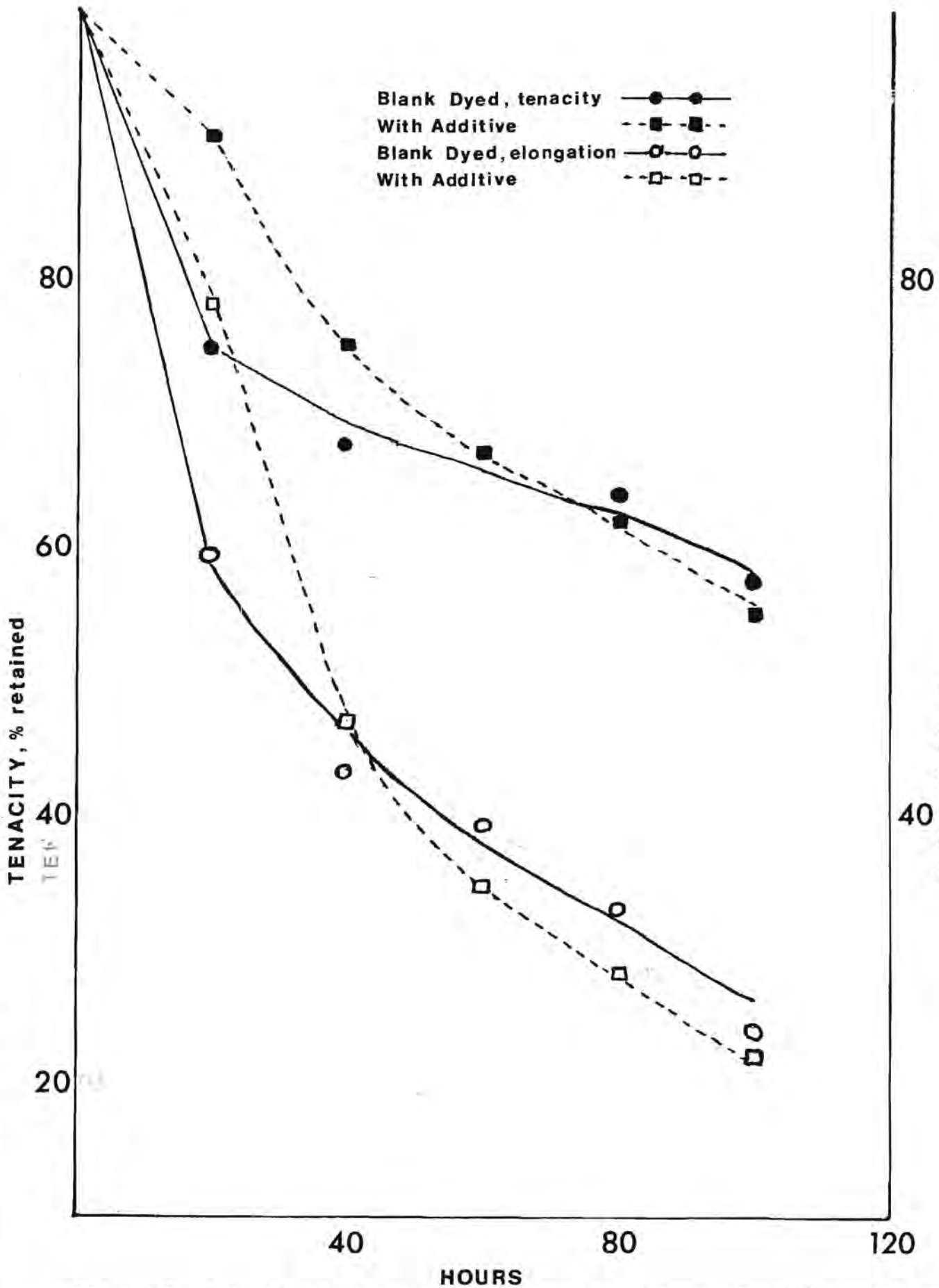


Figure 17. Retention of tenacity and elongation of Nomex Type 433 containing Cyasorb UV-800 compared to control after carbon-arc exposure.

17 Cyasorb UV-[illegible]

absorber apparently stabilizes Nomex during the first 40 hours of exposure but appears to have little effect at longer exposure times. Again the instability of the absorber on exposure may account for these findings.

Of the UV absorbers tested Tinuvin P clearly deserves further investigation.

VI. Conclusions

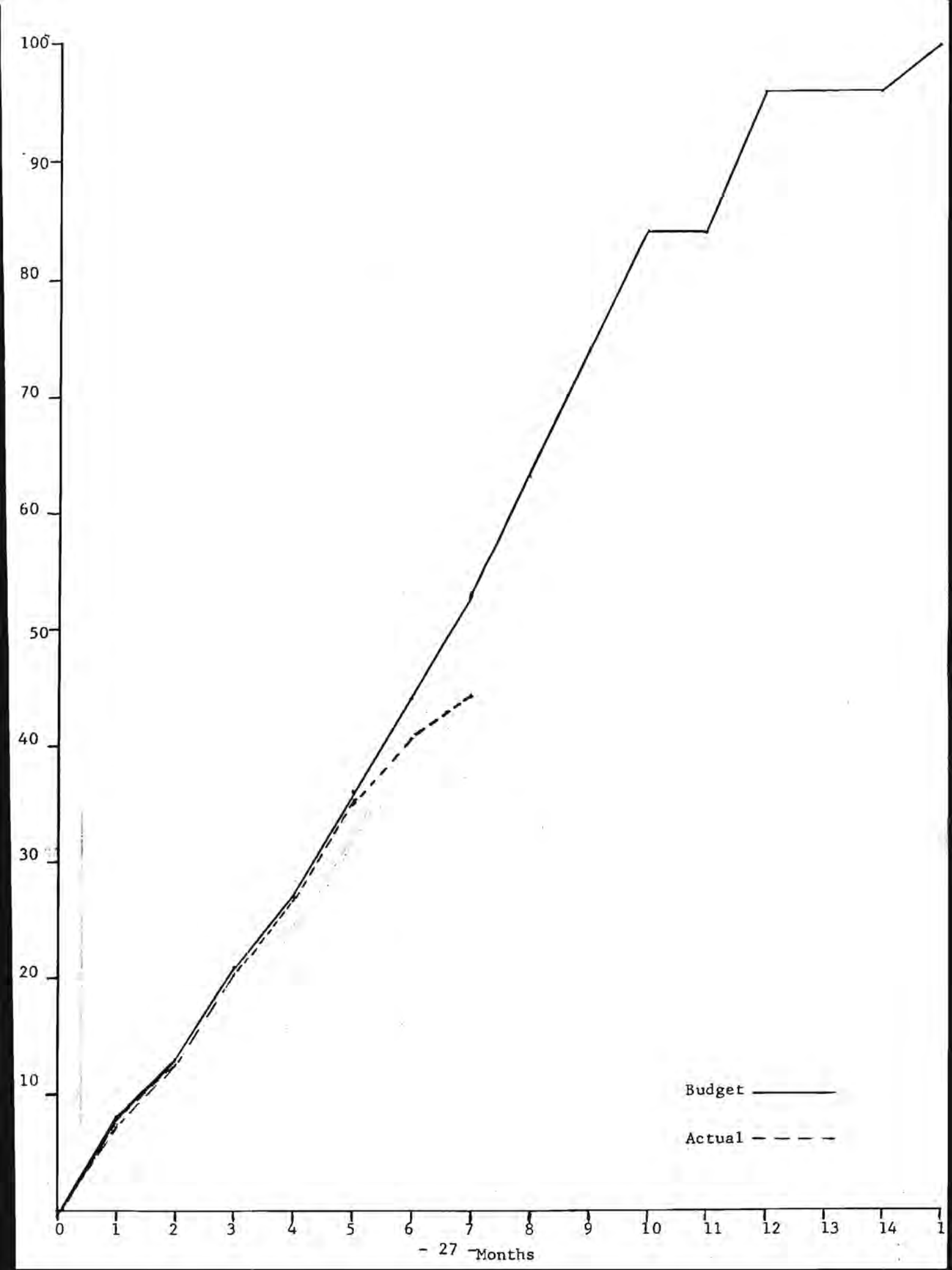
This study of UV screening agents for stabilization of Nomex suggests that some optical brighteners and UV absorbers can have a beneficial effect on Nomex degradation. In both cases the effect is small. However, both Blancophor AW and Tinuvin P should be included in the proposed factorial study to determine if they show synergistic effects with other stabilizing materials.

VII. Future Work

Work is now underway on a number of excited state "quenchers" and data on these materials will be reported next month.

VIII. Budget

The funds budgeted and either expended or allocated for the first seven months are shown on the attached graph.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Monthly Progress Report Number 8

(Jan. 26, 1975 - Feb. 26, 1975)

DEVELOPMENT OF ULTRAVIOLET PROTECTION NOMEX

Life Support SPO
Air Force Systems Command
Aeronautical Systems Division
Wright-Patterson Air Force Base, Ohio 45433

(Prepared Under Contract No. F33657-74-6-0716
by
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SUMMARY

Molecular species capable of accepting energy from excited electronic states can frequently act as stabilizers against UV degradation. These types of materials, called "quenchers" are reported to be effective in aromatic polyamides. Six compounds expected to show quenching behavior have been added to Nomex yarn samples by modified dyeing procedures. One of these, oxanilide, gave improvement in the light stability.

The second meeting to review progress of the research project was held at the Georgia Institute of Technology on February 5, 1975.

Studies on antioxidants and radical scavengers as Nomex stabilizers are now underway.

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I. Introduction

Major efforts this month have been directed toward study of the effects of excited state quenchers in increasing the UV stability of Nomex. These materials are reported to be effective in other aromatic amides but no data is available on their effect in Nomex. Compounds containing metal ions such as zinc and nickel are believed to be particularly effective. One compound of this type, oxanilide, appears promising as a Nomex stabilizer.

II. Quenchers Investigated as Nomex Stabilizers

Six compounds reported to stabilize polymeric systems by a quenching mechanism have been added to Nomex by the modified dyeing procedures reported previously. The compounds investigated are given in TABLE I. All were added to Nomex Type 433 yarn by the modified dyeing procedure described in the January monthly progress report. The levels of additions are being determined by x-ray emission spectroscopy but data are not yet available.

III. Testing and Results

Samples containing quenchers were exposed in the carbon-arc Fade-Ometer for up to 100 hours and exposed and control (blank dyed) samples tested on the Instron.

Retention of tenacity and elongation for samples containing AM-105, IRGASTAB 2002, and Zetax are shown in Figures 1, 2 and 3. All of the compounds containing nickel and zinc apparently reduce both the tenacity and elongation of Nomex on UV irradiation. This result was somewhat surprising in light of

TABLE 1

Quenchers Added to Nomex Yarns

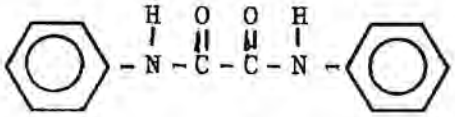
Name	Manufacturer	Chemical Structure
AM-105	Ferro Corp.	Ni Complex Thiobisphenol
GI-10-460	Ciba-Geigy	Ni Containing Experimental Stabilizer
IRGASTAB 2002	Ciba-Geigy	Ni bis[O-Ethyl (3,5 di-tert-butyl-4-HydroxyBenzyl]phosphonat
———	Chem Service	Oxanilide
Zetax	Vanderbilt	2-Mercapto Benzimidazole (Zinc Salt)
NBC	duPont	Nickel Dibutyldithiocarbamate

the reported favorable results with these stabilizers in other aromatic systems.

Results for Nomex yarn containing GI-IO-460 are shown in Figure 4. This is an experimental stabilizer produced by Ciba-Geigy and reported to be a substituted oxanilide. It had no significant effect on the property retention of exposed Nomex yarn.

A similar result was observed for NBC, nickel dibutyldithiocarbamate as shown in Figure 5.

The only "quencher" giving evidence of stabilizing Nomex against UV degradation was oxanilide



Retention of tenacity and elongation after 100 hour exposure to the carbon-arc is shown in Figure 6. Oxanilide appears to give significant improvement in tenacity retention, although retention of elongation is not appreciably affected. Oxanilide has therefore been selected for further study.

There is some question as to the exact way in which oxanilide is acting in stabilizing Nomex. Although considered a "quencher" for excited states, in Nomex the action may really be as a screening agent since oxanilide is a strong absorber in the near UV.

As a group, the quenchers have not shown much effect on the light stability of Nomex.

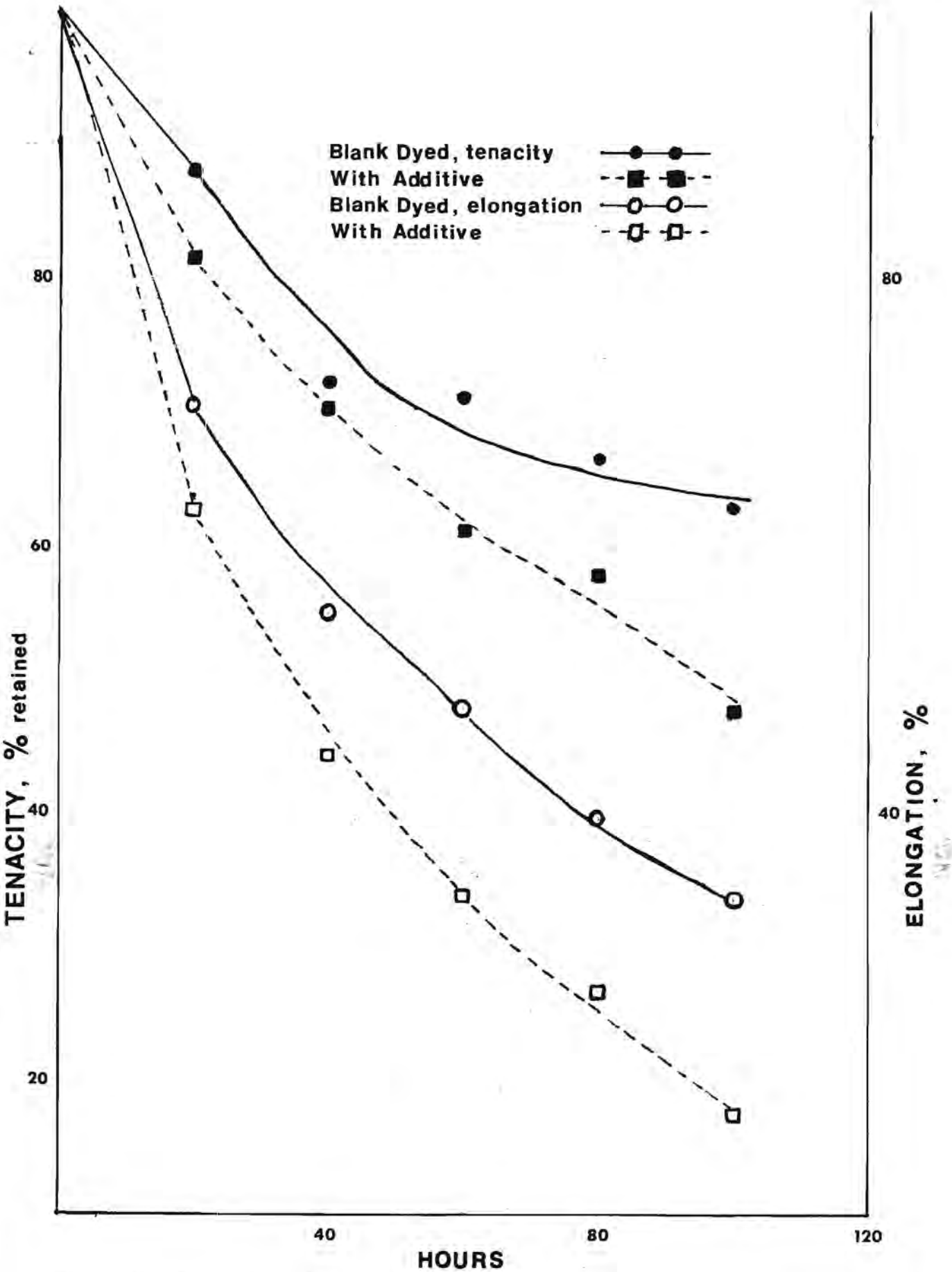


Figure 1. Retention of tenacity and elongation of Nomex Type 433 containing AM-105 compared to blank dyed sample after carbon-arc exposure.

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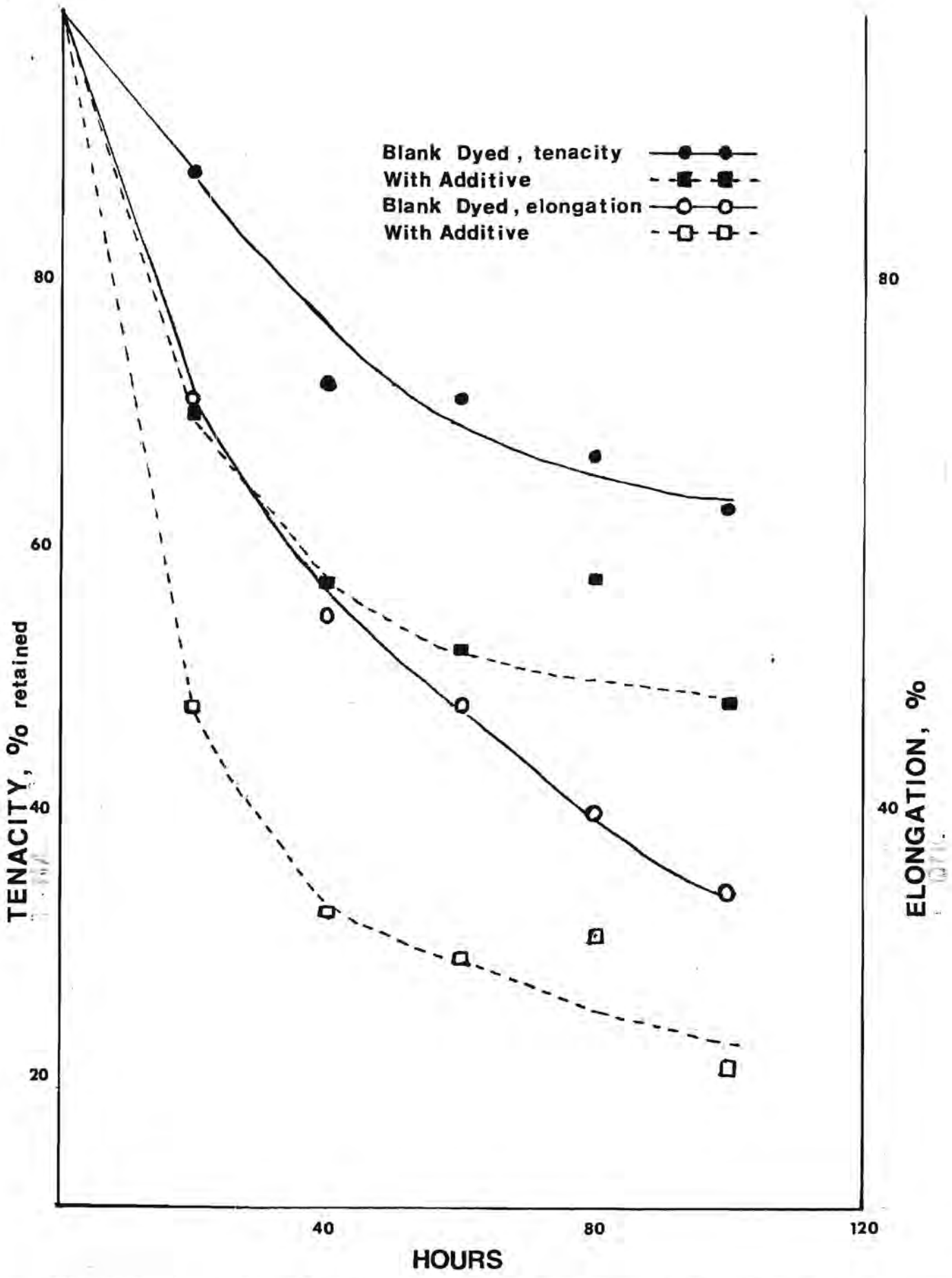

Figure 2. Retention of tenacity and elongation of Nomex Type 433 containing IRGASTAB 2002 compared to blank dyed sample after carbon-arc exposure.

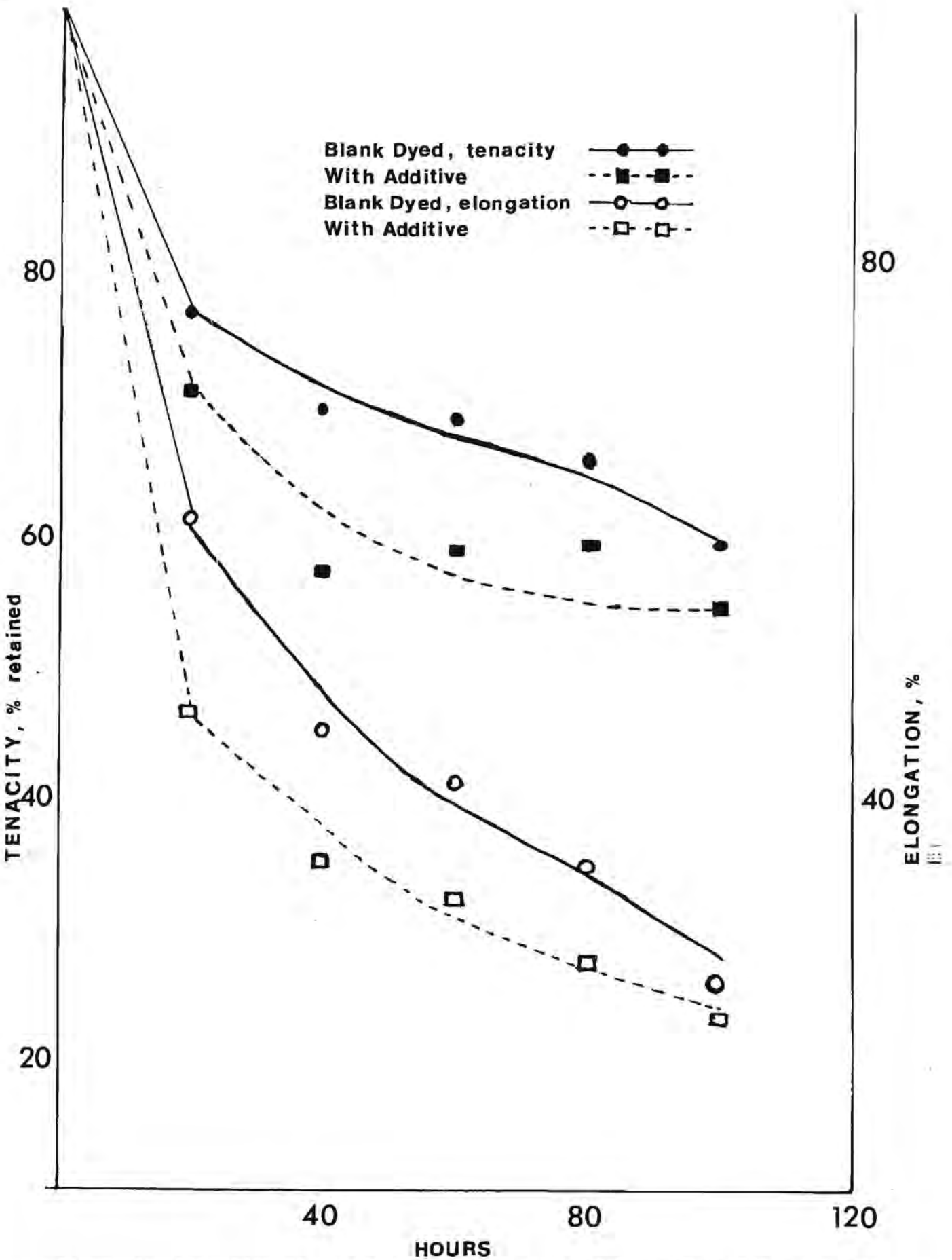

Figure 3. Retention of tenacity and elongation of Nomex Type 433 containing Zetax compared to blank dyed sample after carbon-arc exposure.

3 Zinc Salt

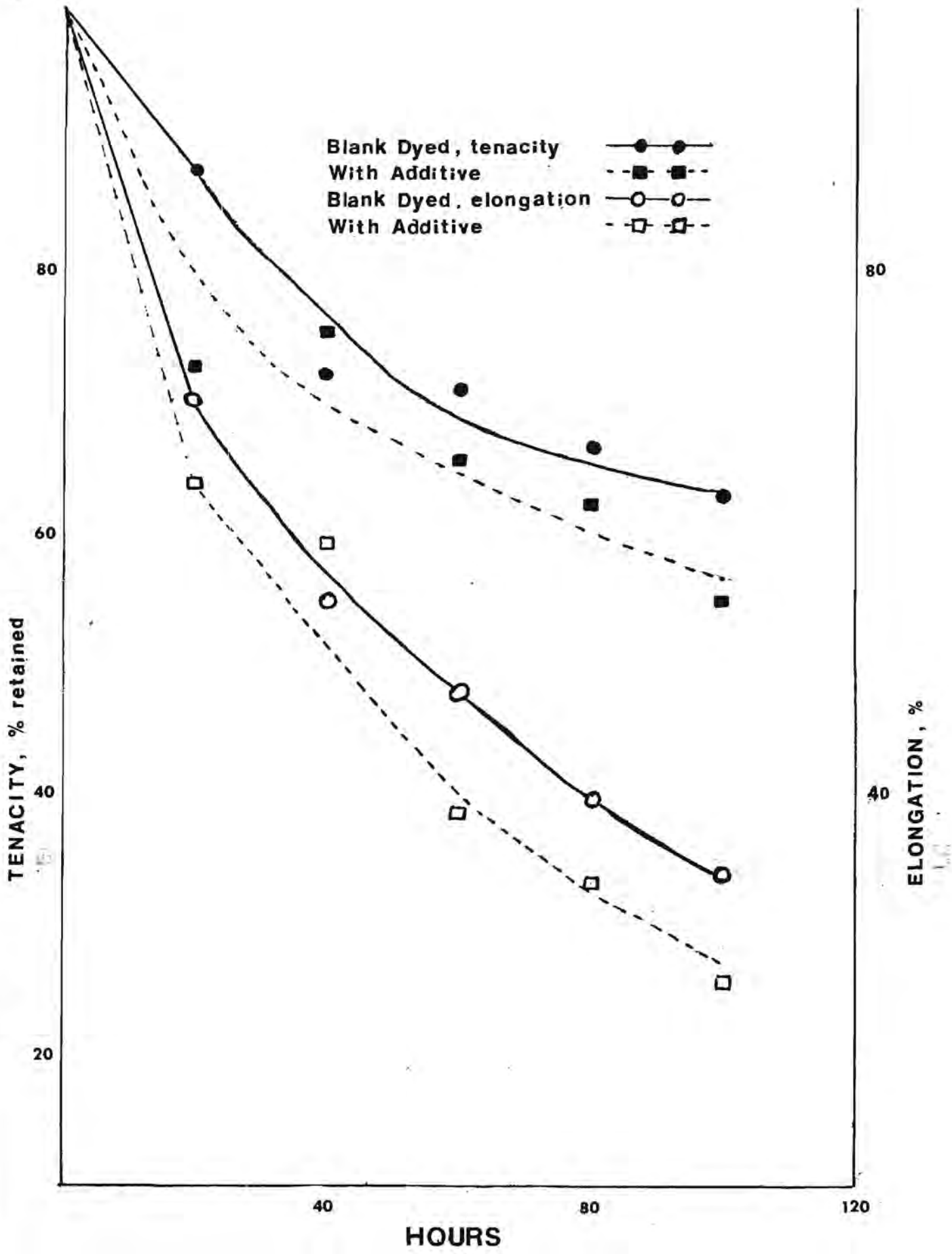

Figure 4. Retention of tenacity and elongation of Nomex Type 433 containing GI-10-460 compared to blank dyed sample after carbon-arc exposure.

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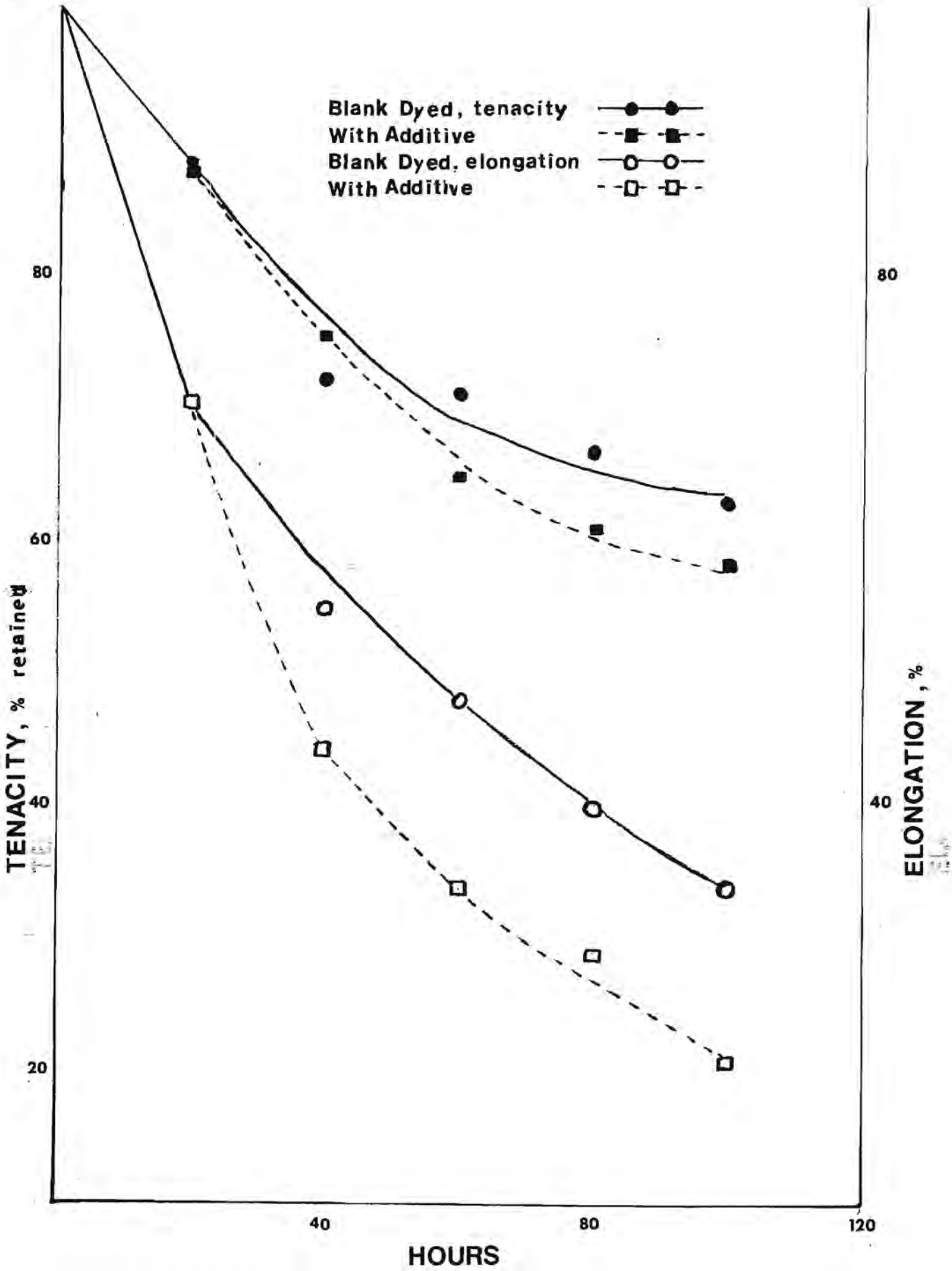


Figure 5. Retention of tenacity and elongation of Nomex Type 433 containing NBC compared to blank dyed sample after carbon-arc exposure.

5 Nickel Dibutyldithiocarbamate

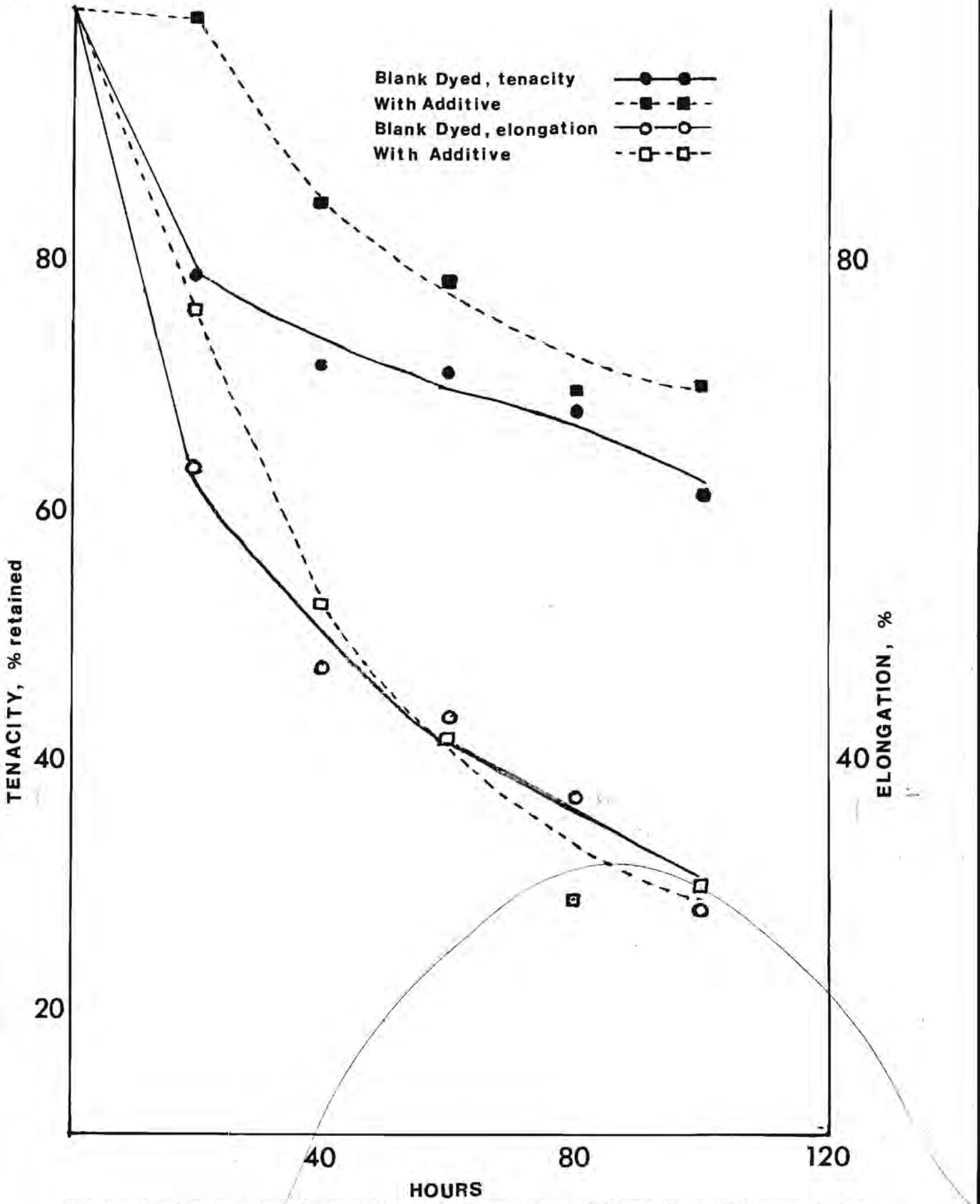


Figure 6. Retention of tenacity and elongation of Nomex Type 433 containing Oxanilide compared to blank dyed sample after carbon-arc exposure.

6 Oxanilide

IV. Technical Review Meeting

The second technical review meeting was held at the Georgia Institute of Technology on February 5. A status report was presented by personnel engaged on the project and a tour of laboratory and testing facilities was conducted. The monitor, Mr. Gloor, called attention to a new patent recently issued which reports that osmium tetroxide and iodates in combination improve the light stability of Nomex. This lead will be pursued.

The status of the project in terms of the milestone chart presented at the initiation of the project was discussed and it was generally agreed that the project is approximately 1 to 1½ months behind the planned schedule. This situation resulted from delays in obtaining Nomex yarn initially and to equipment problems with the xenon-arc Fade-Ometer.

It was generally agreed that closer contacts between research personnel and the contract monitor would be desirable as we enter the middle phase of the project.

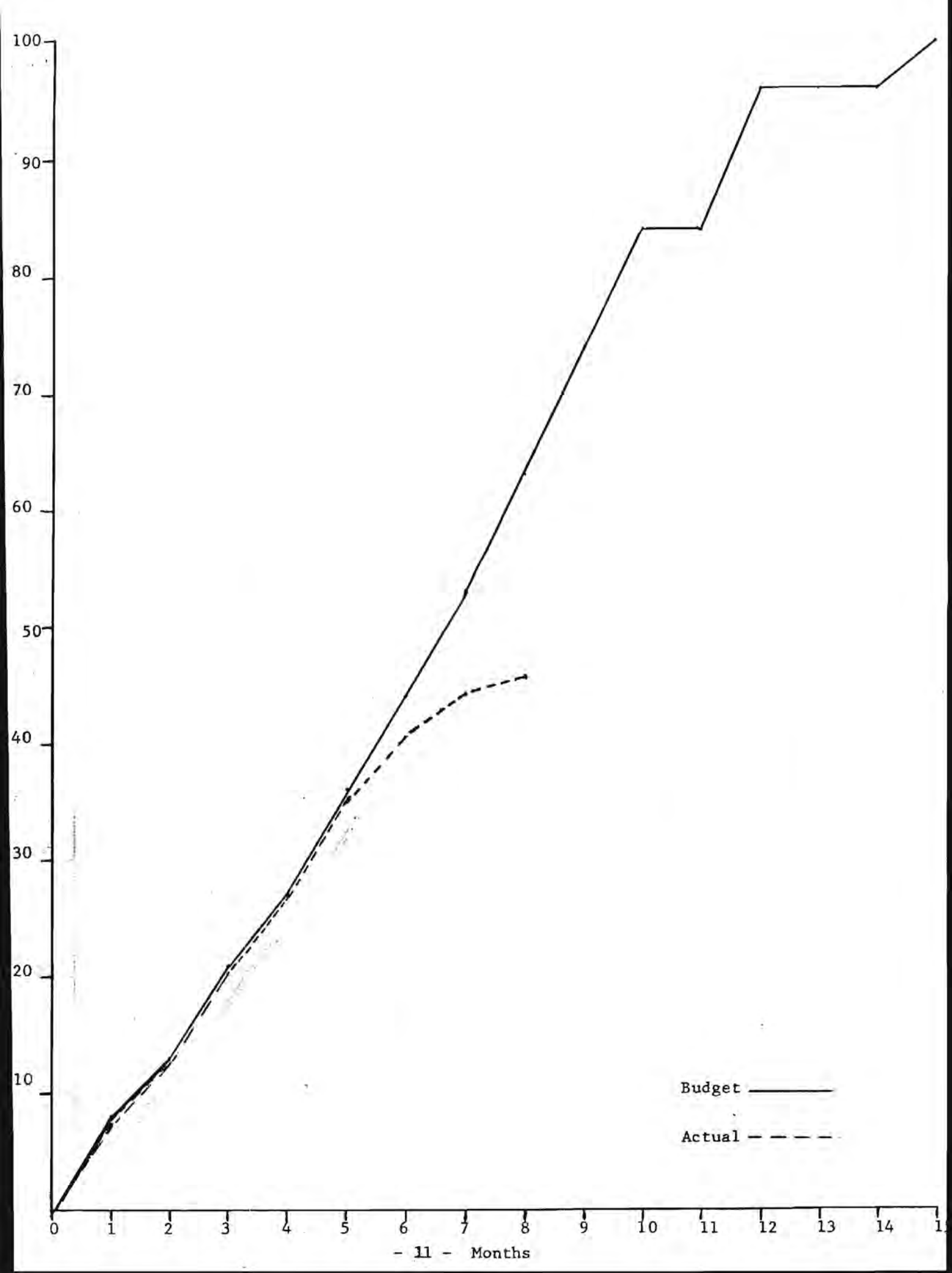
The third technical review meeting is planned for April, 1975, at Wright-Patterson Air Force Base.

V. Future Work

Samples containing anti-oxidants have been prepared and are under test. Results for this class of stabilizers will be reported next month.

VI. Budget

The Funds budgeted and either expended or allocated for the first eight months are shown on the attached graph.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E-27-623

Monthly Progress Report Number 9
(Feb. 26, 1975 - Mar. 26, 1975)

DEVELOPMENT OF ULTRAVIOLET PROTECTION NOMEX

Life Support SPO
Air Force Systems Command
Aeronautical Systems Division
Wright-Patterson Air Force Base, Ohio 45433

(Prepared Under Contract No. F33657-74-6-0716
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Summary

Several commercially available antioxidants have been examined this month to determine their effectiveness in reducing UV degradation of Nomex. None of these materials were effective in improving Nomex stability.

Previous experiments had suggested that reactions with polymer chain end groups might be an effective approach to Nomex stabilization. Further investigation of this approach has not been encouraging.

Of the classes of stabilizers examined to date only UV screening agents have proven effective in reducing Nomex UV degradation. Further studies on several of these materials are underway.

Table of Contents

I. Introduction

In previous monthly reports work on the effectiveness of UV screening agents and excited state quenchers for stabilizing Nomex has been described. Work this month has concentrated on an evaluation of antioxidants for reducing Nomex UV degradation.

II. Antioxidants as Nomex UV Stabilizers

The antioxidants investigated in this study are listed in Table 1. These materials were added to Nomex yarn Type 433 by the dyeing procedures described previously. The antioxidants selected are of the hindered phenol type with other structural features designed to inhance the antioxidant characteristics.

Samples of yarn containing the antioxidants were exposed to the carbon-arc Fade Ometer for periods up to 100 hours. Tenacity and elongation of the yarn samples were determined before and after exposure.

The per cent retention of tenacity and elongation for samples containing Irganox 1035 is shown in Figure 1. This antioxidant gives no perceptible difference in the stability of Nomex.

Similar results for samples containing Plastanox 1735, Irganox 1010, and Irganox 1098 are shown in Figures 2, 3 and 4. All of these antioxidants reduce the stability of Nomex slightly. The reasons for this effect are not known at the present time.

The results of these studies in conjunction with previously reported studies on sulfur compounds suggest that antioxidants as a class show little promise as stabilizers for Nomex. Since these materials are primarily effective in free radical oxidative degradation reactions, the results at

Table 1

Antioxidants Added to Nomex Yarn

Name	Manufacturer	Type
Irganox 1010	Ciba-Geigy	Ester containing H.P.
Irganox 1035	Ciba-Geigy	Sulfur containing H.P.
Irganox 1098	Ciba-Geigy	Amide Containing H.P.
Plastanox 1735	American Cyanamide	Hindered Phenol

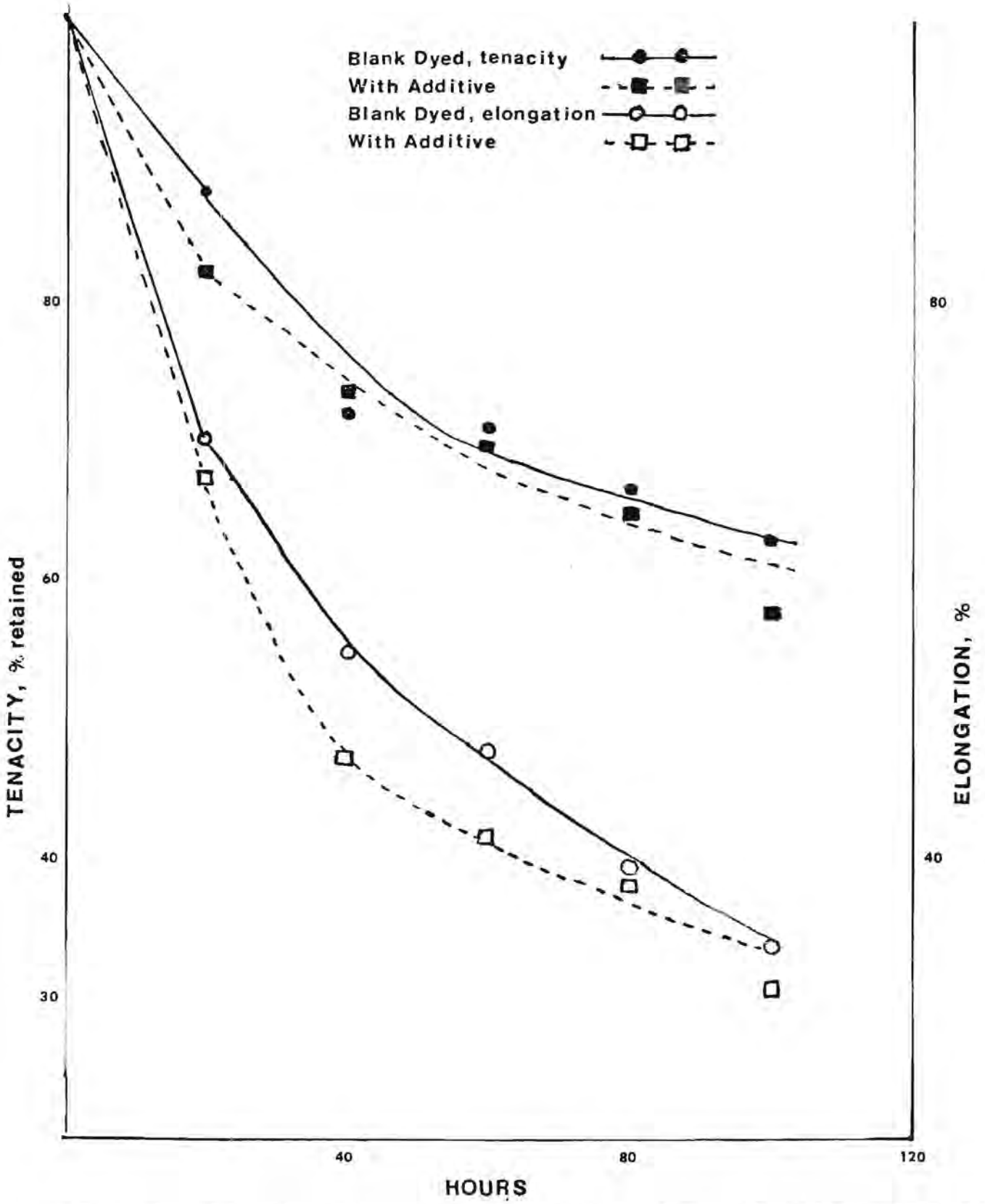


Figure 1 -- Retention of tenacity and elongation of Nomex Type 433 containing Irganox 1035 compared to control sample after Carbon-arc exposure.

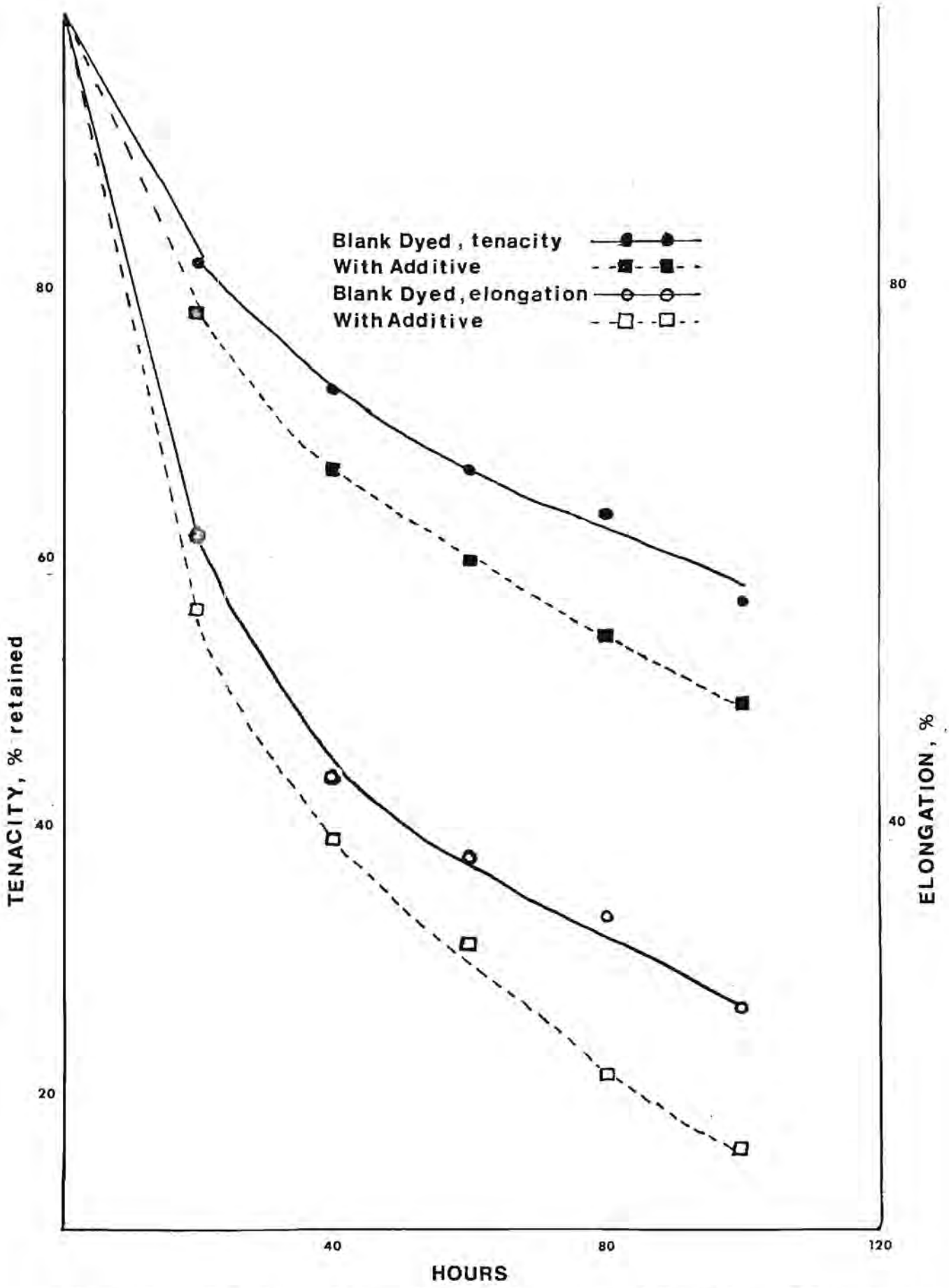


Figure 2 - - Retention of tenacity and elongation of Nomex Type 433 containing Plastanox 1735 compared to control sample after Carbon-arc exposure.

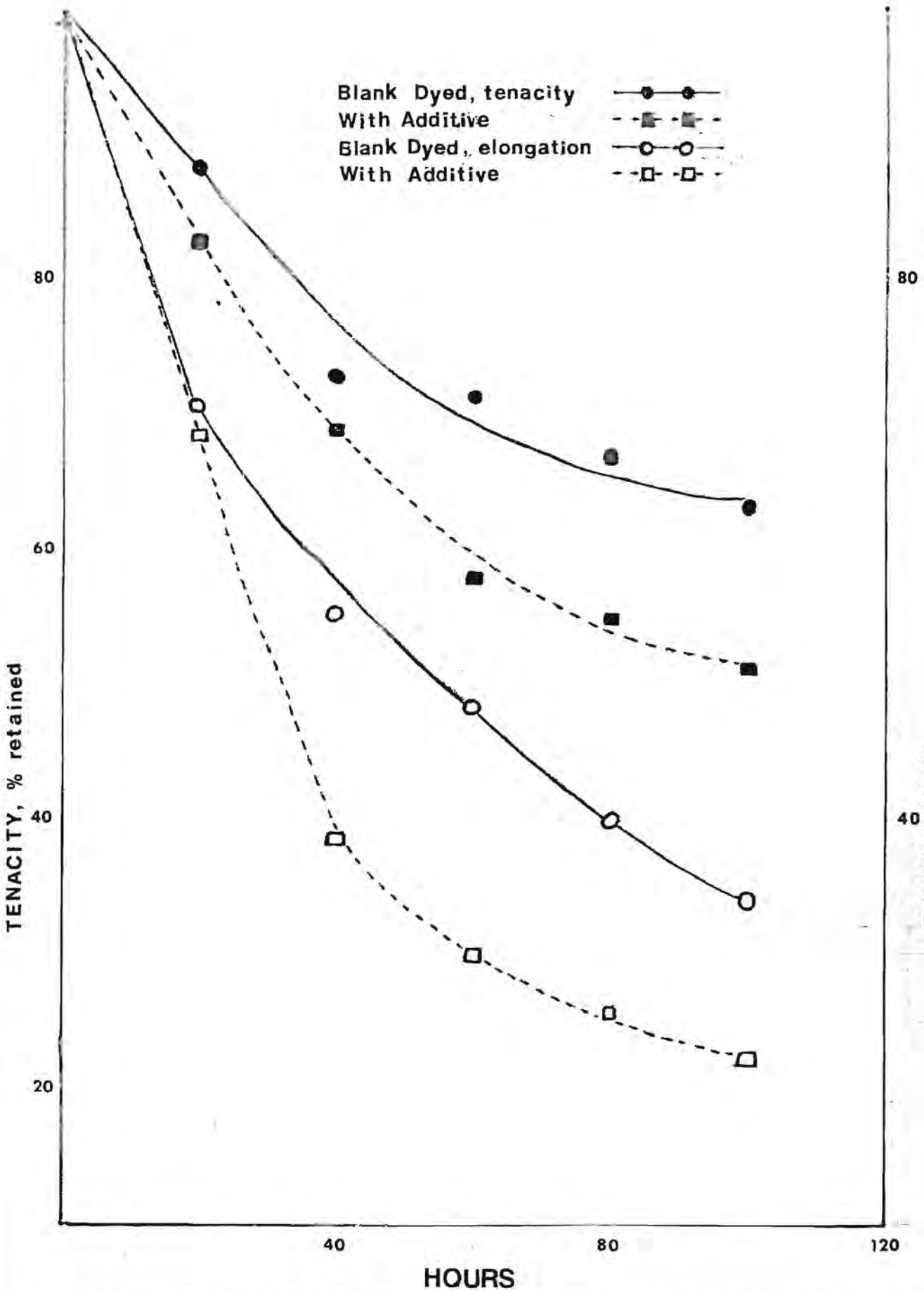


Figure 3 - - Retention of tenacity and elongation of Nomex Type 433 containing Irganox 1010 compared to control sample after Carbon-arc exposure.

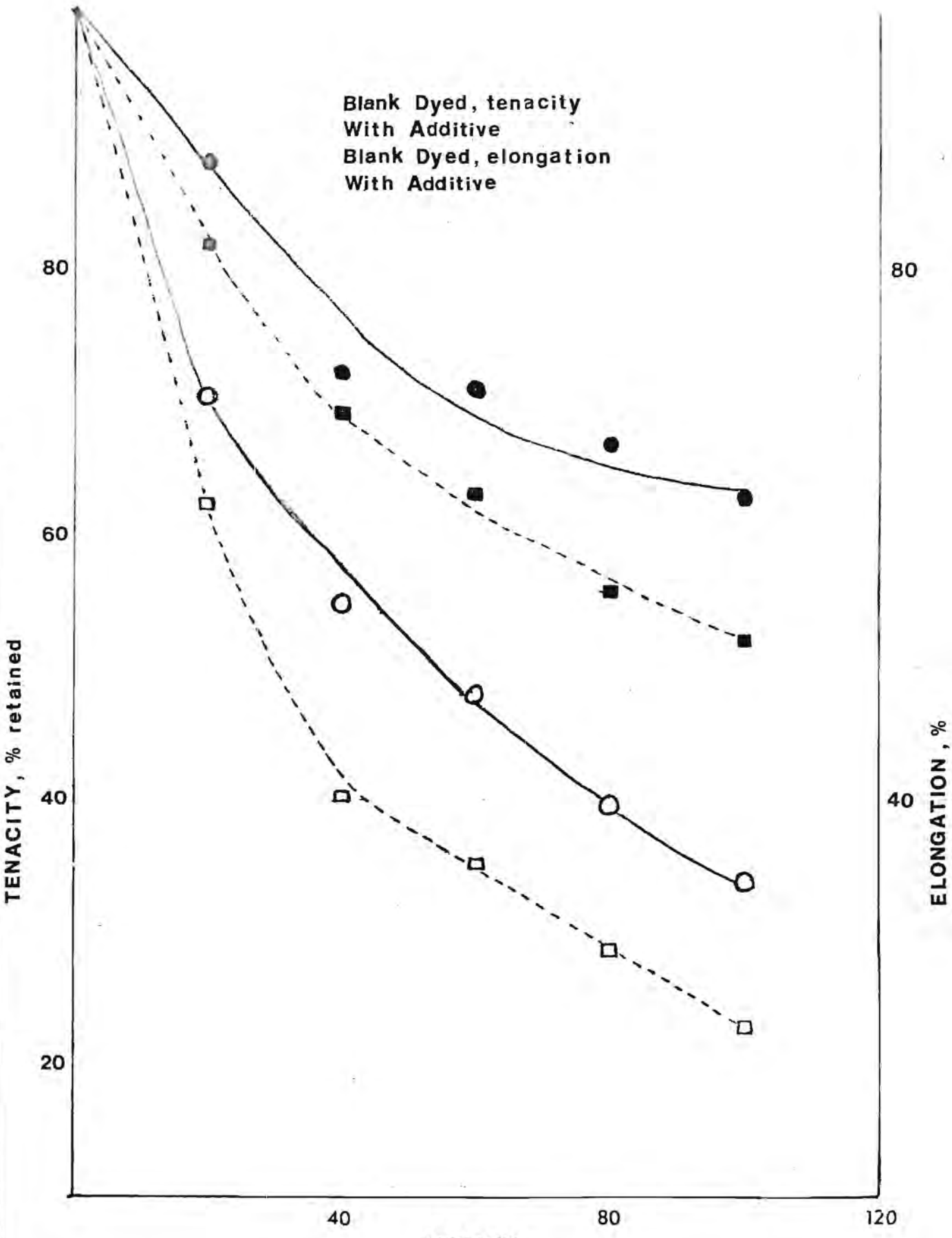


Figure 4- -. Retention of tenacity and elongation of Nomex Type 433 containing Irganox 1098 compared to control sample after Carbon-arc exposure.

least indicate that such reaction mechanisms are not involved in Nomex UV degradation.

III. End Group Reactions for Nomex Stabilization

Some previous experiments had suggested that amine end groups in Nomex may contribute to the UV degradation. An experiment was therefore designed to determine if reactions with amine end groups would increase Nomex stability.

Aromatic amines in the presence of nitrous acid react to form diazonium salts which readily react with phenols to produce diazo compounds. These reactions are used extensively in preparation of the diazo class of dyestuffs and were used to reduce the number of amine end groups in a sample of Nomex yarn.

The yarn samples were first treated with nitrous acid in the presence of a carrier. They were then treated with beta oxynaphthoic acid. Formation of the colored diazo compound gave evidence that the aromatic amine end groups were undergoing reaction.

Samples with reacted amine end-groups were exposed to the carbon-arc Fade Ometer and compared with control samples. Results are shown in Figure 5. These results suggest that reduction in amine end group content does not provide greater stability to Nomex yarn.

IV. Future Work

UV screening agents are the only class of stabilizers that have proven effective thus far for Nomex stabilization. Other screening agents are now under investigation in an attempt to find the best materials for use

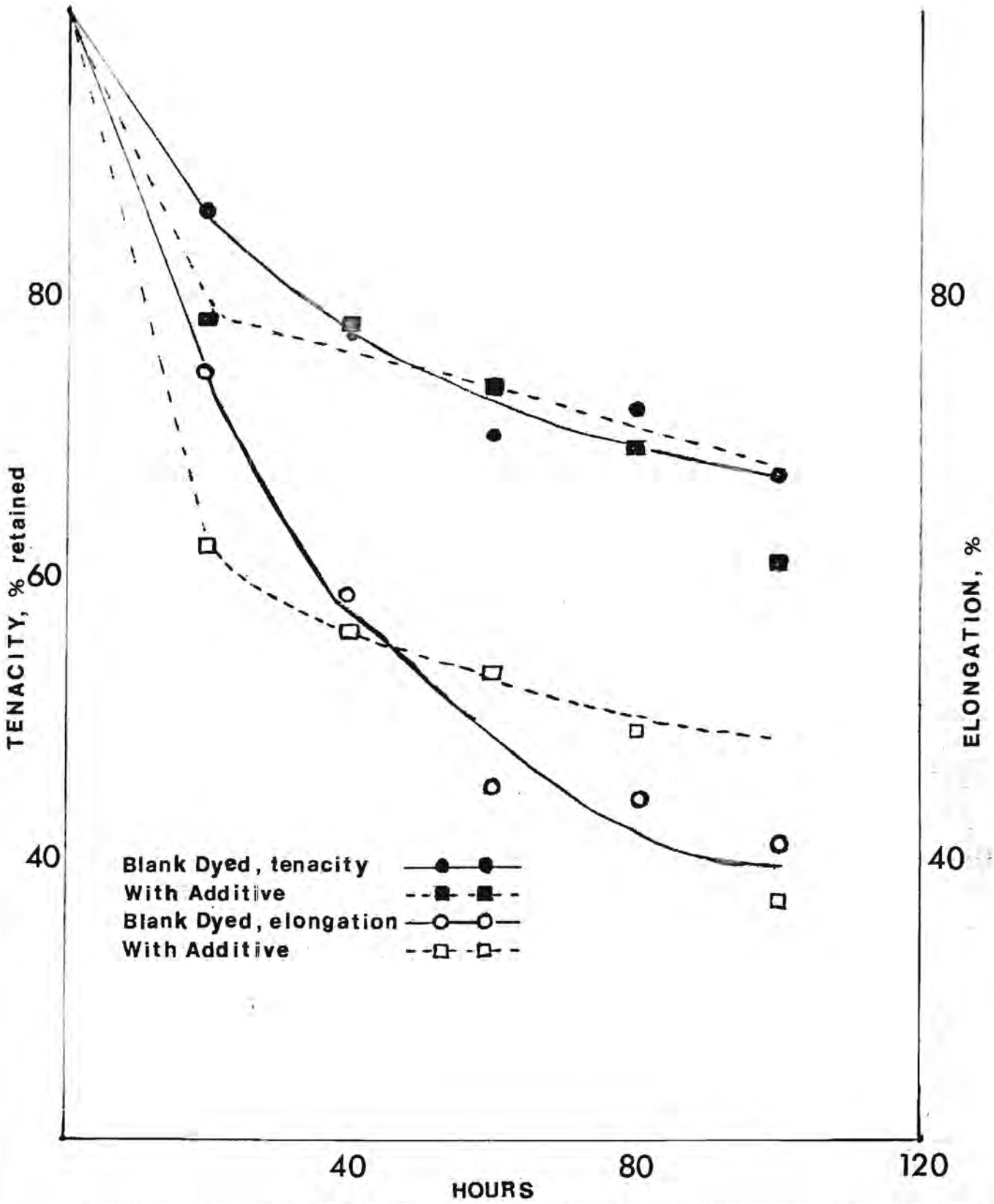
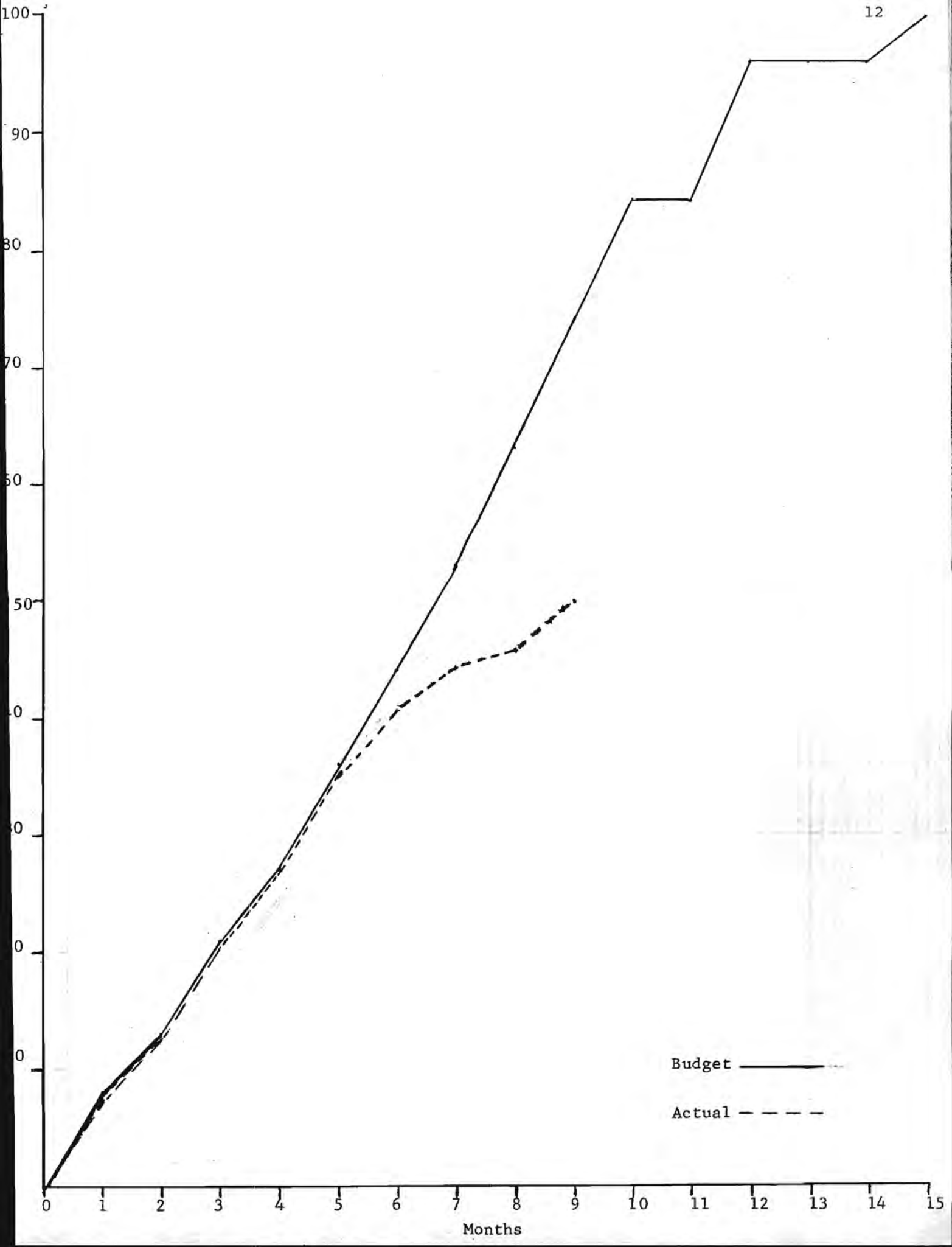


Figure 5 - - Retention of tenacity and elongation of Nomex Type 433 with end groups reacted with beta-oxynaphthoic acid compared to control sample after Carbon-arc exposure.

in development of the stabilizer system.

V. Budget

The funds budgeted and either expended or allocated for the first nine months are shown on the attached graph.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E-27-623

Monthly Progress Report Number 10

(Mar. 26, 1974 - Apr. 26, 1974)

Development of Ultraviolet Protection Nomex

Life Support SPO
Air Force Systems Command
Aeronautical Systems Division
Wright-Patterson Air Force Base, Ohio 45433

(Prepared Under Contract No. F33657-74-C-0716
by
Georgia Institute of Technology
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Summary

Initial experiments to discover materials capable of reducing the UV degradation of Nomex are essentially complete. Of the large number of materials screened, only three have shown consistant, benefial effects when incorporated in Nomex fibers. These three - Blancophor AW, Tinuvin P and Oxanilide - have been added to both sage green and natural Nomex and exposed to both carbon-arc and xenon-arc sources. Results are reviewed in this report.

The third technical review meeting is planned for May 13, 1975.

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I. Introduction

Screening experiments on possible additives for improving the UV stability of Nomex are essentially complete. Three materials - Blancophor AW, Tinuvin P, and oxanilide-gave improvement in retention of Nomex properties after exposure to light. These materials have been investigated in greater detail and results of these studies are reviewed in this report.

II. Blancophor AW

Blancophor AW is a commerciably available optical brightener of the aminocoumarin type produced by GAF. It was initially tested by addition to Nomex Type 433 yarn by the dyeing procedures previously described and exposure in the carbon-arc Fade - ometer. It gave improvement in retention of both tenacity and elongation as indicated in Figure 1. A similar sample has also been tested in the xenon-arc Fade - ometer and the results are shown in Figure 2. This experiment confirms that the Blancophor AW is stable even in the presence of a light source (such as the xenon-arc) with high UV output.

Carbon-arc exposures have also been conducted on Nomex Type 430 yarn containing Blancophor AW. Results are shown in Figure 3. The effectiveness of this stabilizer candidate is even more pronounced in the white Nomex than in the sage green.

In all experiments conducted to date Blancophor AW has increased retention of both tenacity and elongation of Nomex yarn. This compound has been selected for the planned factorial experiment.

III. Tinuvin P

Tinuvin P is a UV screening agent of the benzotriazole type produced

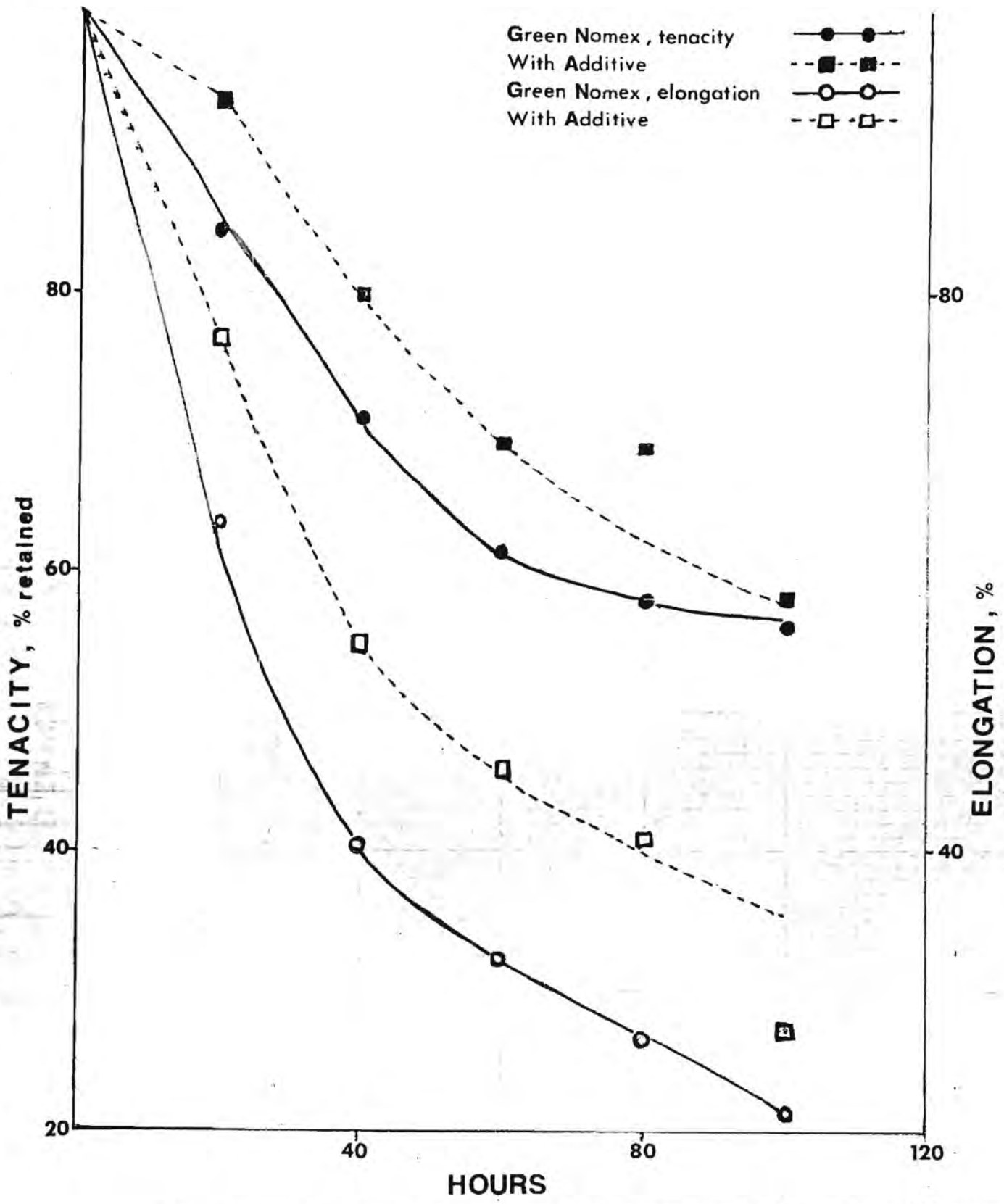


Figure 1 -- Retention of tenacity and elongation of Nomex Type 433 containing Blancophor AW compared to control sample after carbon-arc exposure.

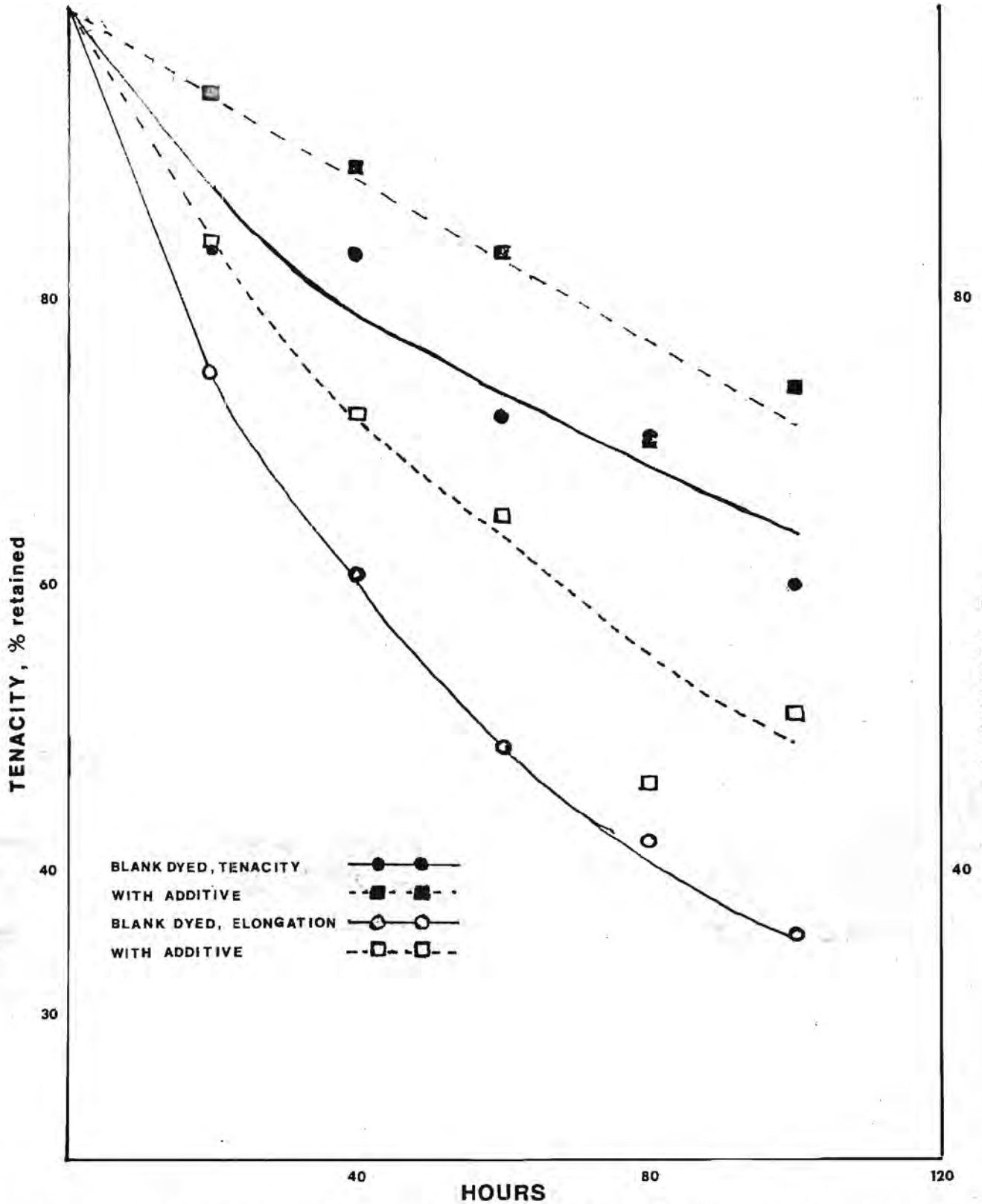


Figure 2-- Retention of tenacity and elongation of Nomex Type 433 containing Blancophor AW compared to control sample after xenon-arc exposure.

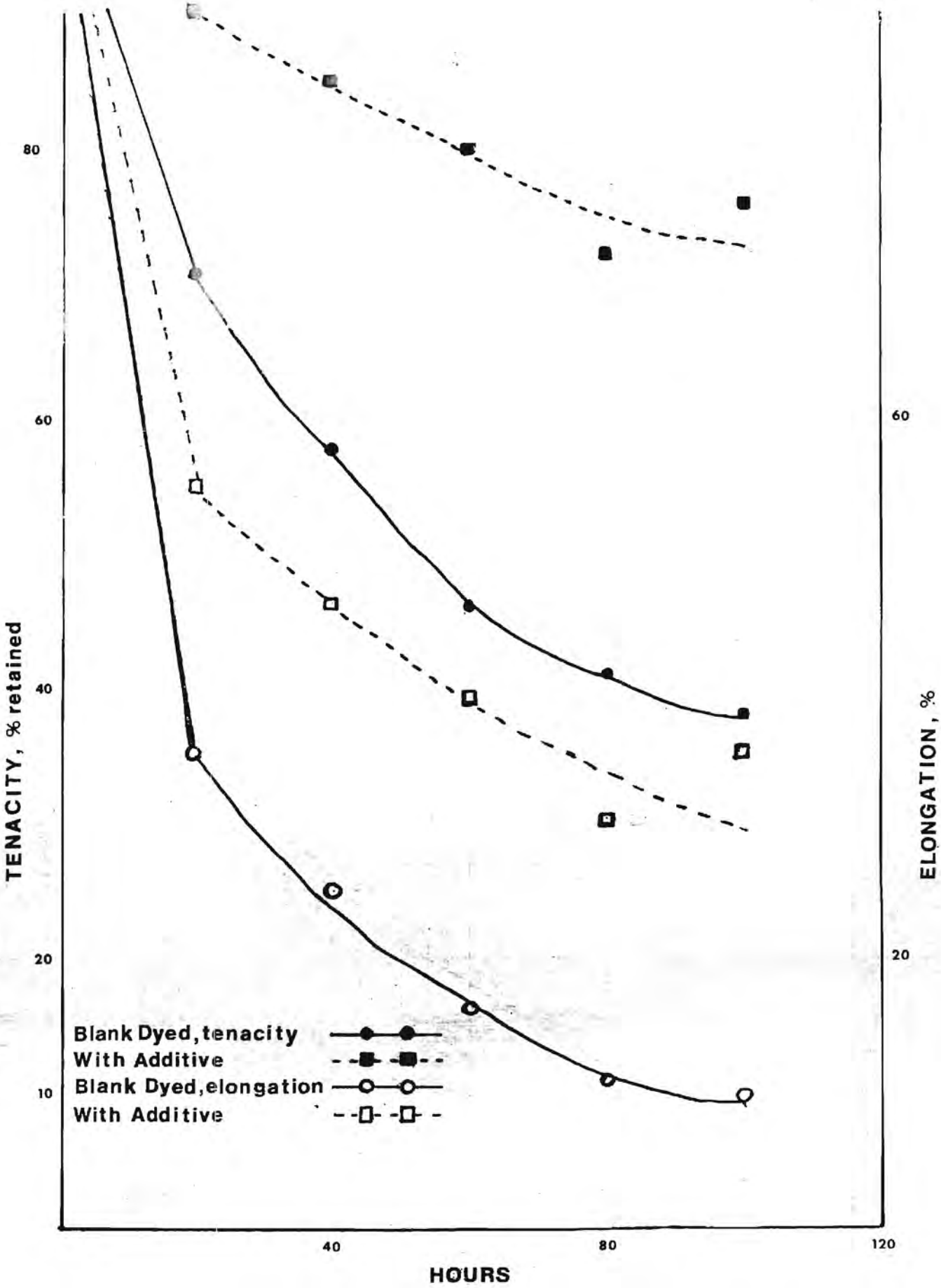


Figure 3-- Retention of tenacity and elongation of Nomex Type 430 containing Blancophor AW compared to control sample after carbon-arc exposure.

by the CIBA-GEIGY Company. It has been reported to be a stabilizer for Nomex but the results have not been consistent. Tinuvin P was added by dyeing procedures to Nomex Type 433 and the yarn samples exposed in the carbon-arc Fade - ometer. Although the improvements were not as large as with Blancophor AW, Figure 4 shows that retention of both tenacity and elongation were increased by the additive. Results of similar studies on Nomex Type 433 exposed in the Xenon-arc Fade - ometer and Nomex Type 430 exposed in the carbon-arc Fade - ometer are shown in Figures 5 and 6. These results suggest that Tinuvin P should be part of the planned factorial experiment.

IV. Oxanilide

Oxanilide is the diamide produced by reaction of oxalic acid with aniline. It is sometimes used as a "copper inhibitor" in stabilizer formulations for polymers. Result of exposure in the carbon-arc Fade - ometer of Nomex Type 433 yarn containing oxanilide is shown in Figure 7. Similar results for Xenon-arc exposure are shown in Figure 8. These results are interesting in that oxanilide has little effect on retention of elongation on exposure to UV light but does give improvement in retention of tenacity.

The mechanism by which oxanilide stabilizes Nomex is not known. It was thought that oxanilide might be an effective screening agent but absorption spectra do not show a strong peak in the region responsible for Nomex degradation. It is possible therefore that oxanilide may stabilize Nomex by a different mechanism. It could therefore show a synergistic effect in the presence of the other stabilizers. Oxanilide will be included in the factorial experiment.

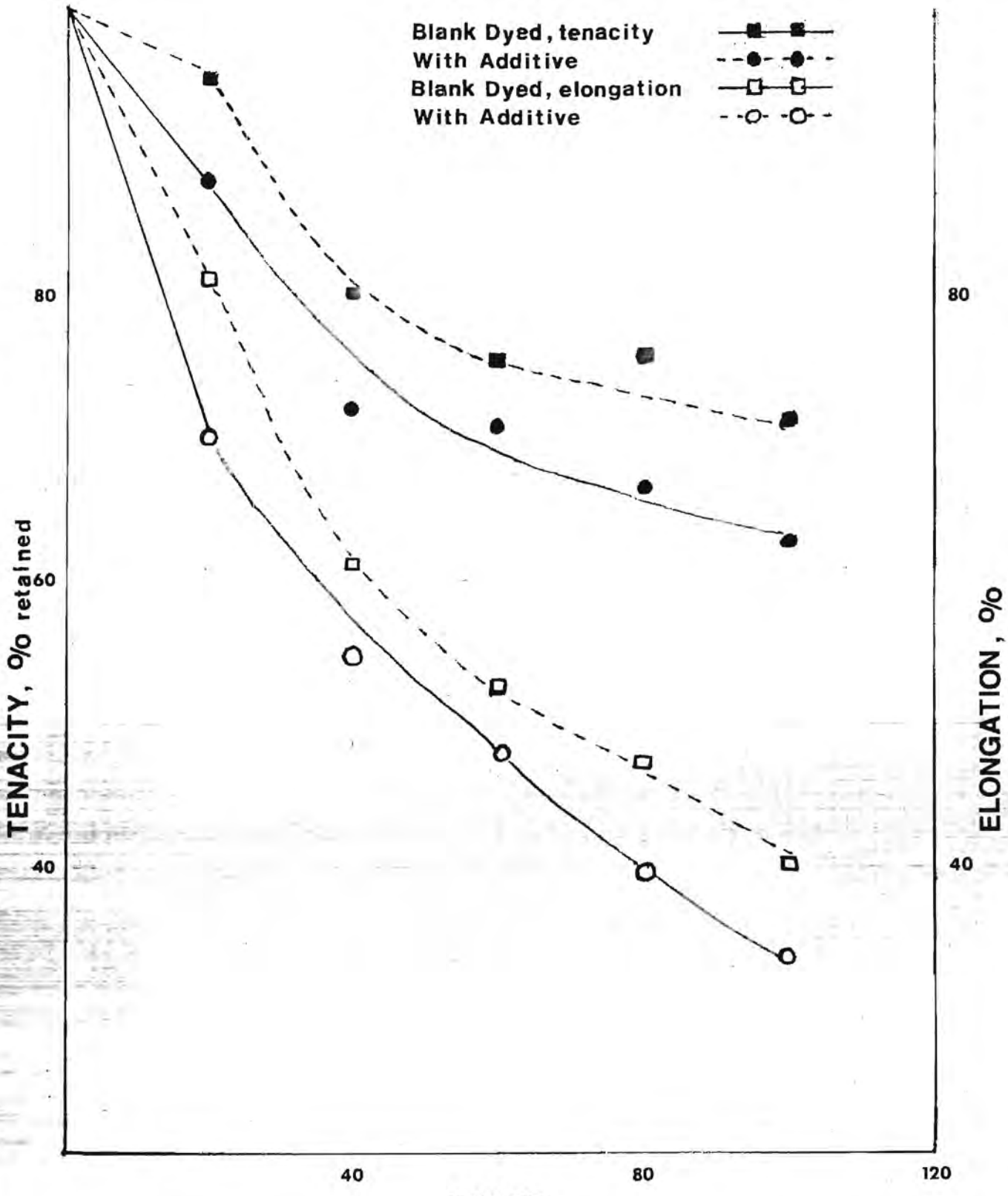


Figure 4-- Retention of tenacity and elongation of Nomex Type 433 containing Tinuvin P compared to control after carbon-arc exposure.

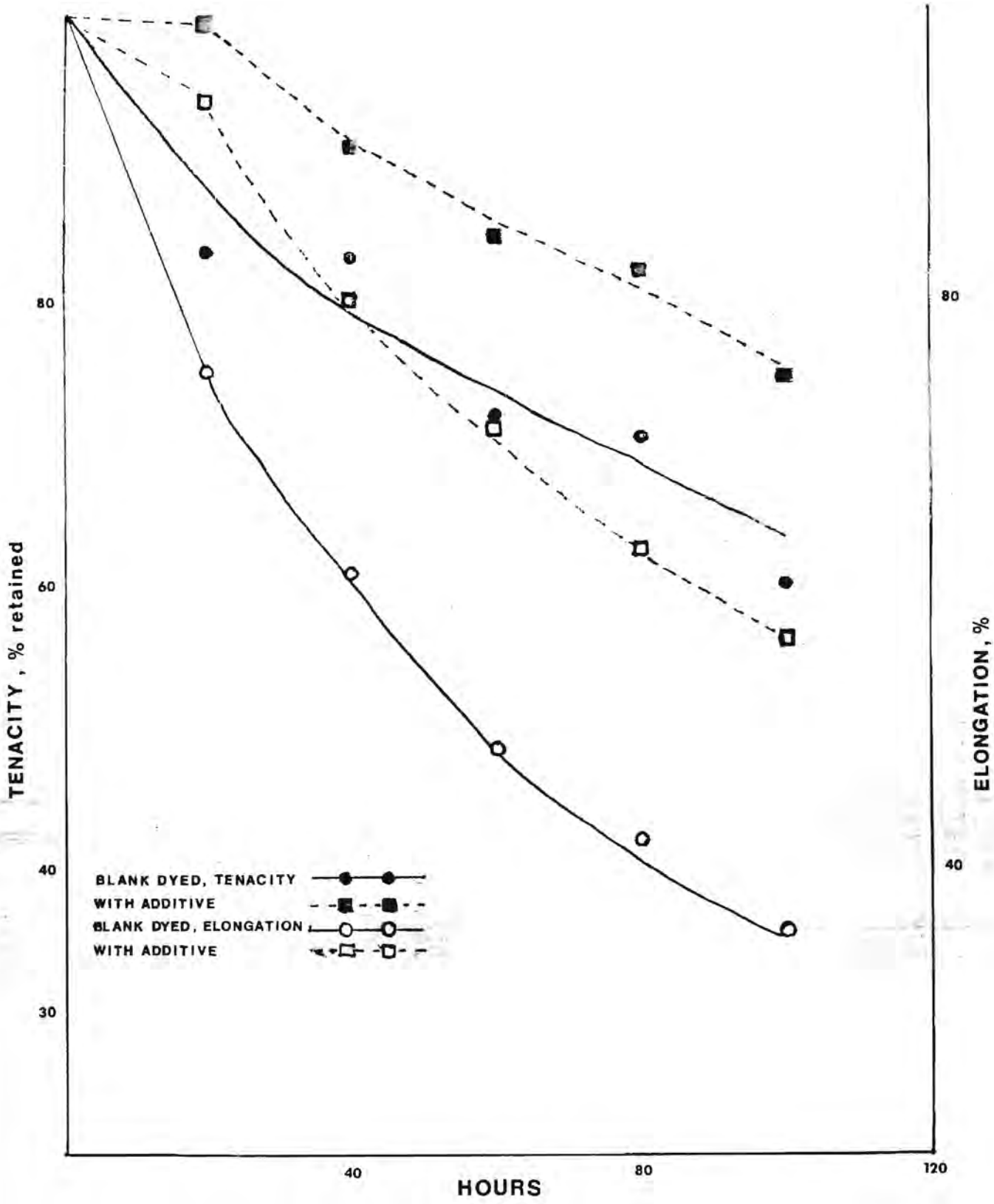


Figure 5-- Retention of tenacity and elongation of Nomex Type 433 containing Tinuvin P compared to control after Xenon-arc exposure.

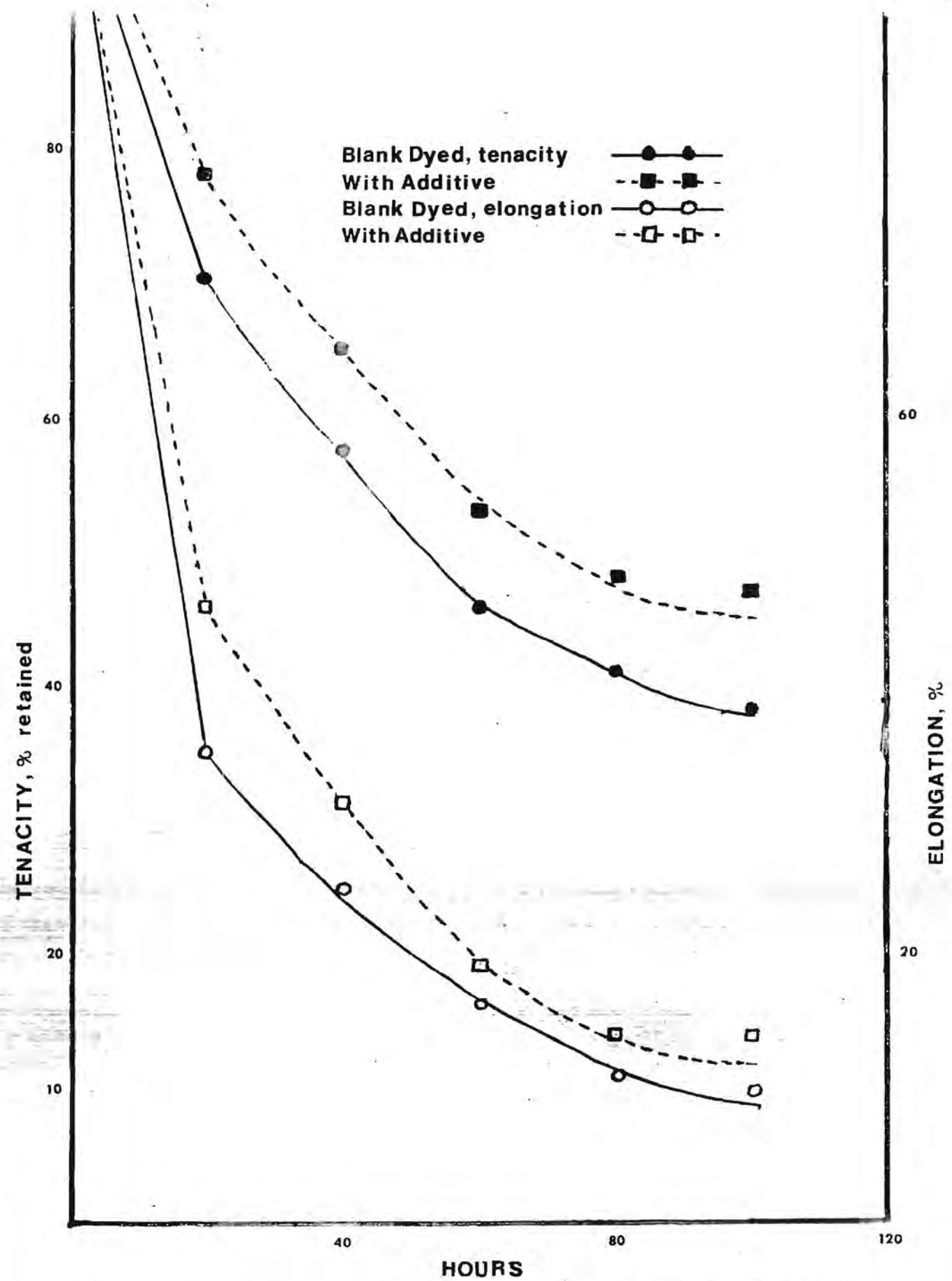


Figure 6-- Retention of tenacity and elongation of Nomex Type 430 containing Tinuvin P compared to control after carbon-arc exposure.

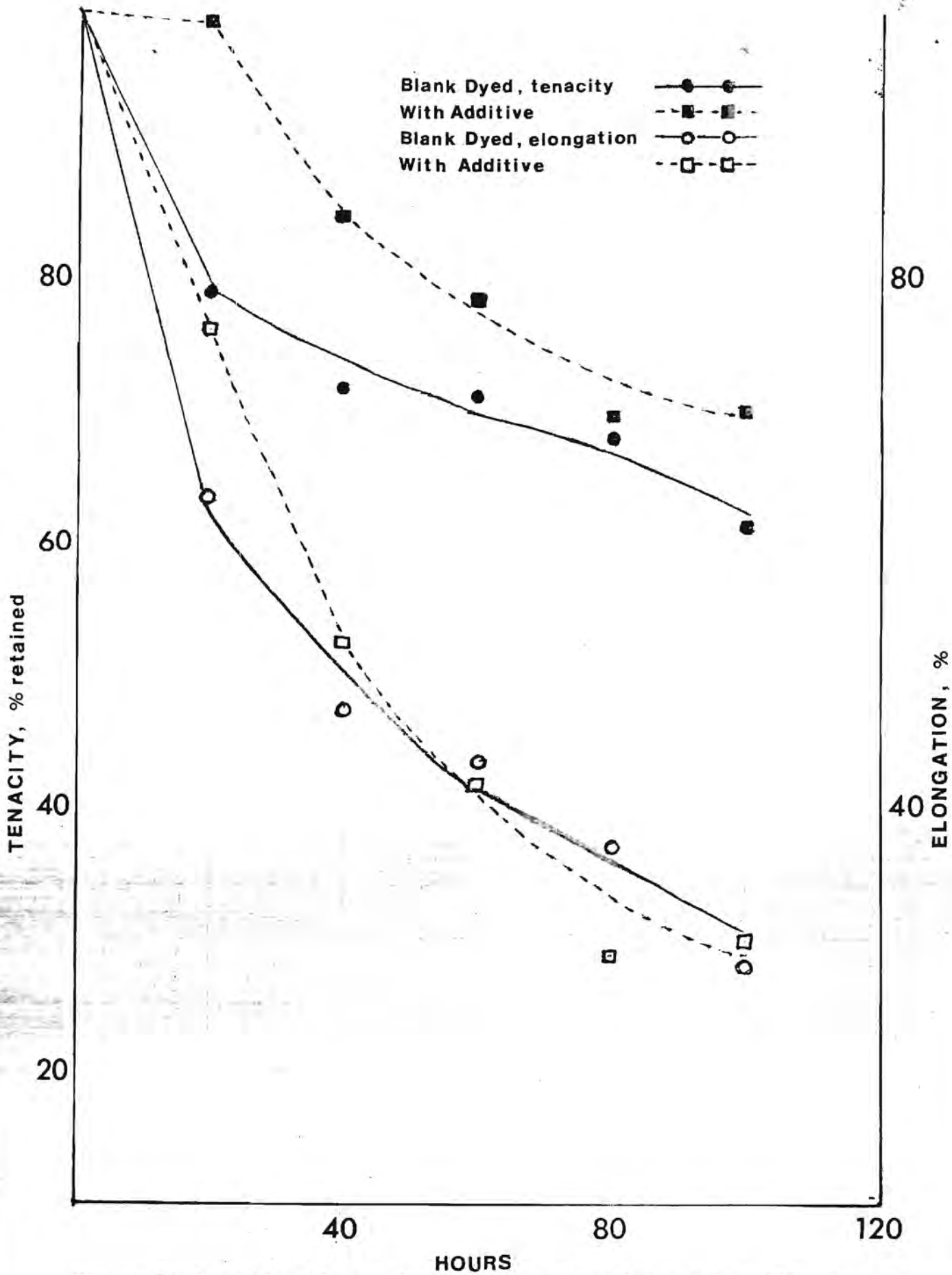


Figure 7-- Retention of tenacity and elongation of Nomex Type 433 containing Oxanilide compared to blank dyed sample after carbon-arc exposure.

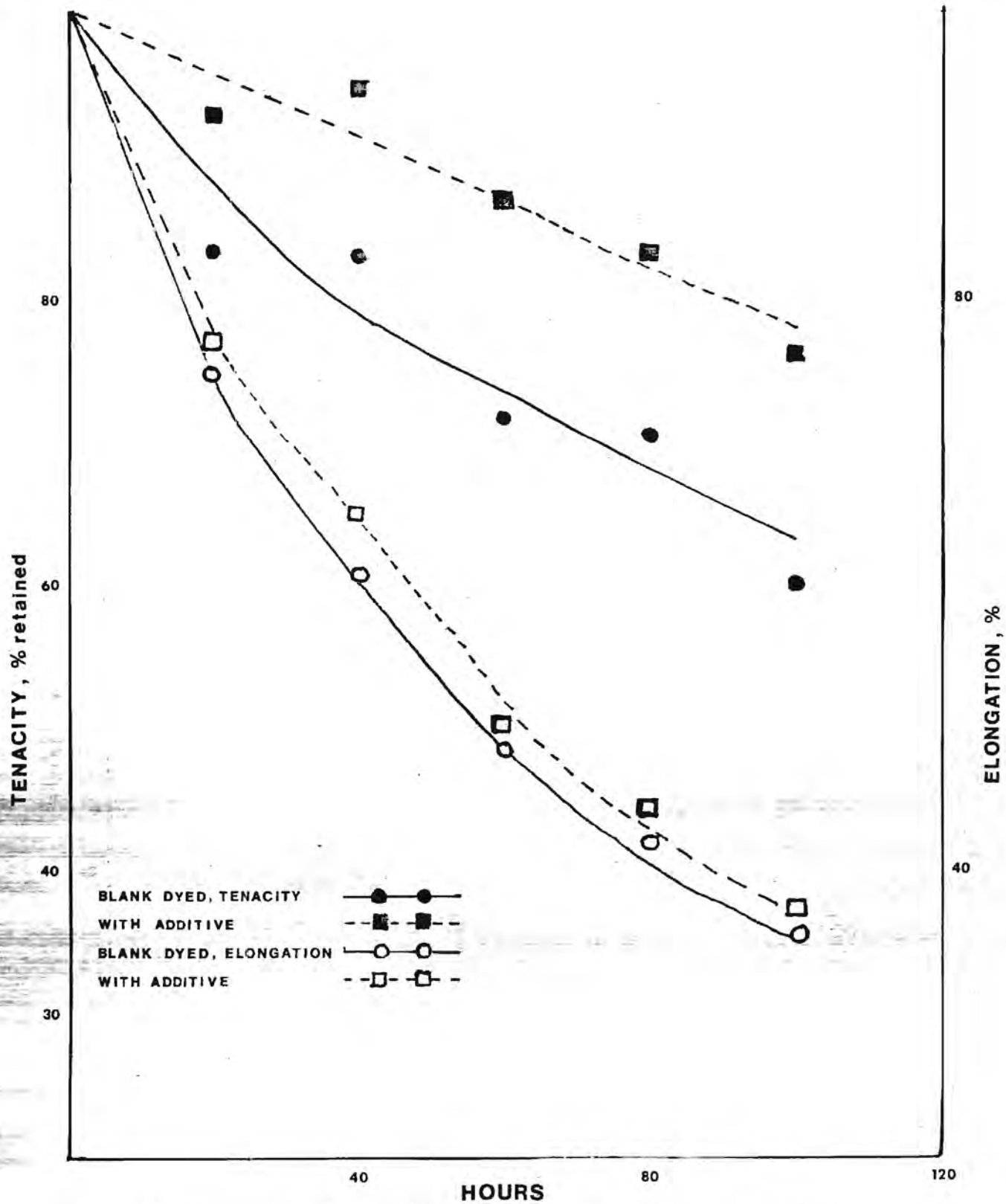


Figure 8-- Retention of tenacity and elongation of Nomex Type 433 containing Oxanilide compared to blank dyed sample after xenon-arc exposure.

V. Other UV Screening Agents

At least 2 of the 3 stabilizers for Nomex probably act by competing with the substrate for the available photons. One other UV screening agent of a different chemical structure than the benzotriazoles was therefore studied. Eastman Inhibitor RMB (Resorcinol Monobenzoate) which rearranges to give 2,4 - dihydroxybenzophenone was added to Nomex and the samples exposed to the carbon-arc Fade - ometer. Results are shown in Figure 9. These results suggest that benzophenone type stabilizers do not appear to be effective on Nomex.

VI. Third Technical Meeting

The third technical review meeting will be held at Wright-Patterson Air Force Base on May 13. The purpose of this meeting is to establish details of the planned factorial experiment.

VII. Budget

The funds budgeted and either expended or allocated for the first ten months are shown on the attached graph.

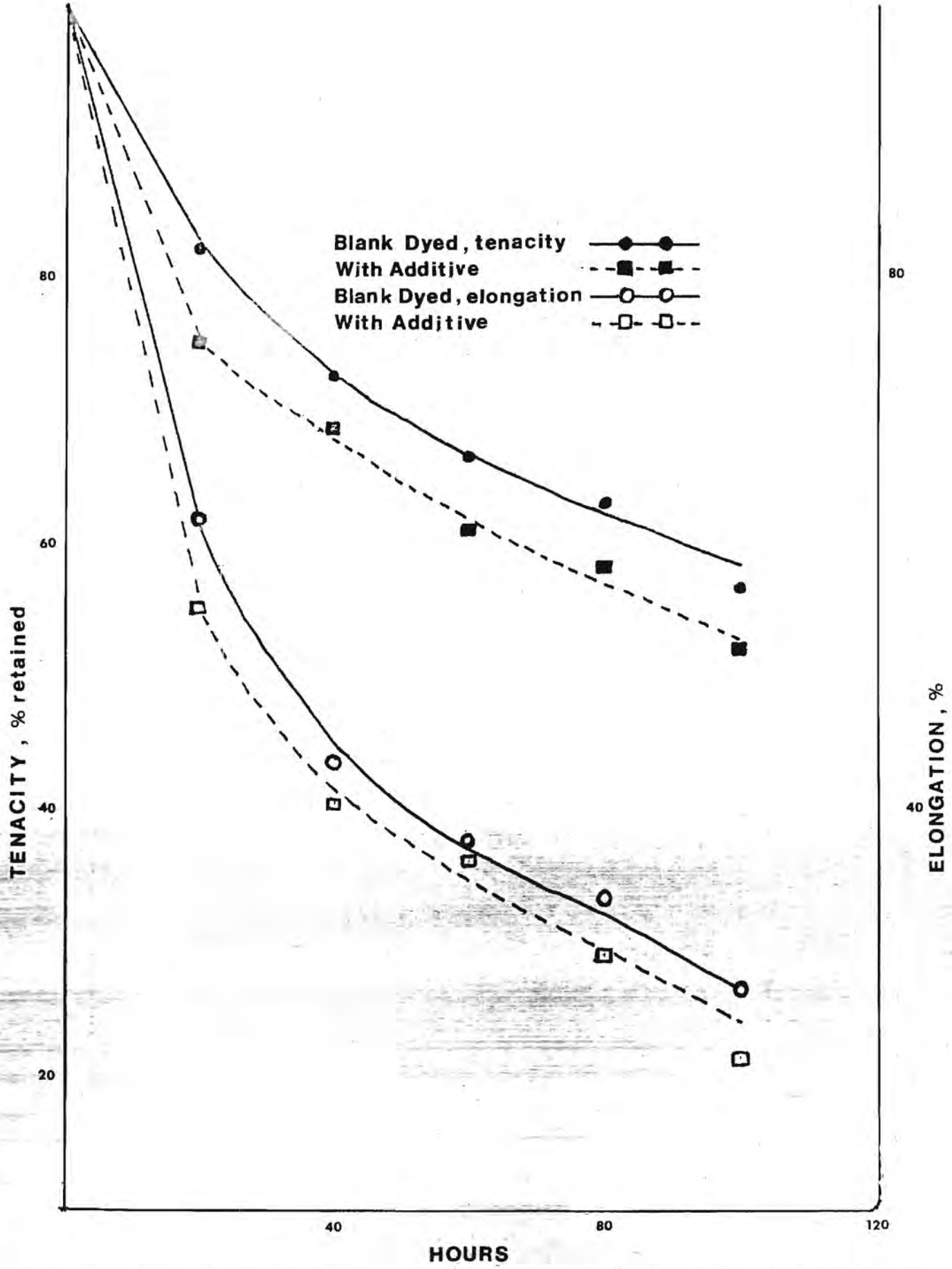
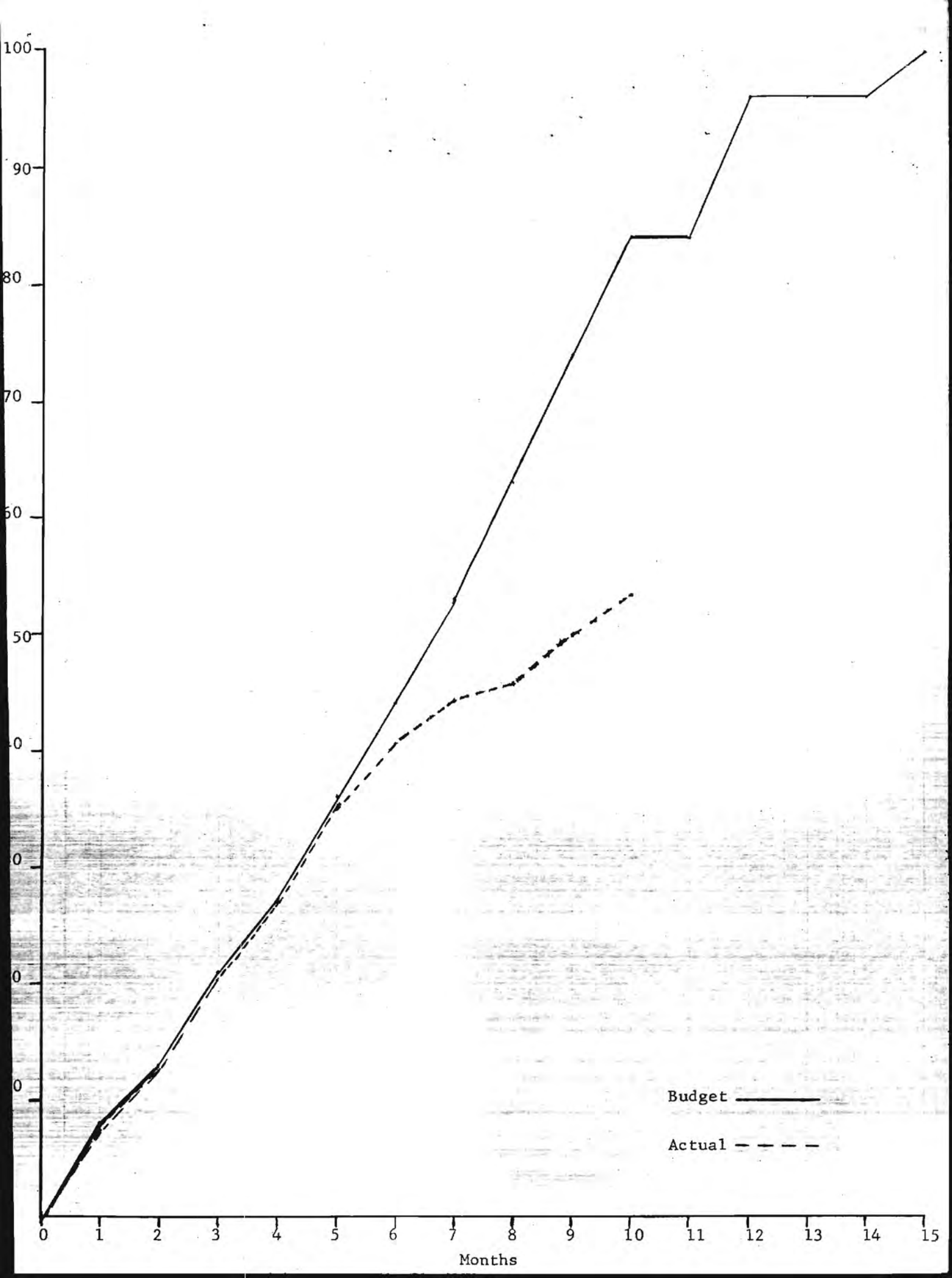


Figure 9 -- Retention of tenacity and elongation of Nomex Type 433 containing Eastman Inhibitor RMB compared to blank dyed sample after carbon-arc exposure.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E-27-623

Monthly Progress Report Number 11

(Apr. 26, 1975 - May 26, 1975)

Development of Ultraviolet Protection Nomex

Life Support SPO
Air Force Systems Command
Aeronautical Systems Division
Wright-Patterson Air Force Base, Ohio 45433

(Prepared Under Contract No. F33657-74-C-0716
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Summary

The third technical review meeting was held on May 13, 1975 at Wright-Patterson Air Force Base. The factorial experiment for selection of UV stabilizer systems was discussed and agreement was reached on details of the experimental work. The factorial experiment will be conducted on fabric (Mil-C-38351, Type II, Class 1) woven of color-sealed Nomex sage green yarn.

Initial experiments have been conducted on UV degradation of fabric samples in preparation for the factorial experiment. Loss of breaking strength and elongation in the warp direction and loss of breaking strength in the fill direction on UV exposure follow very similar curves. Somewhat greater loss of elongation in the filling direction is observed.

Methods for quantitative determination of the amounts of stabilizers present in fabric samples have been developed for use in the factorial experiment.

Table of Contents

I. Introduction

Major effort this month has been directed toward preparations for the factorial experiment for selection of stabilizer systems to be investigated in Phase II of the project. This has included development of analytical methods for stabilizers and procedures for exposure and testing of Nomex fabric samples.

Experiments were also begun to determine the effects of Tinuvin P and Blancophor AW on E-11, a new experimental thermally resistant yarn produced by Dupont.

II. Technical Review Meeting

The third technical review meeting was held at Wright-Patterson Air Force Base on May 13, 1975. Present at the meeting were Walter Gloor, Stanley Schulman, Jack Ross, Lee Brock and Wayne Tincher. The purpose of the meeting was to review results of the screening program and to confirm details of the planned factorial experiments.

It was decided that three stabilizers - - Blancophor AW, Tinuvin P and Oxanilide - - would be investigated at 4 levels - - 0, 33, 66, and 100% OWF. Fabric samples (Mil-C-38351, Type II, Class 1) of color-sealed Nomex sage green yarn will be used for the test. Prepared samples will be exposed to the carbon-arc fadeometer for periods of 0, 20, 40, 60, and 100 hours and tested by the 1" ravel strip method. Samples will be tested in the warp direction only as this is the direction of maximum stress in the design of articles produced from Nomex fabrics.

A new Dupont yarn designated E-11 which is expected to replace Nomex in some applications was also discussed at the meeting. This yarn is believed to be a fiber blend of regular Nomex and HT-4. It was decided that the stabilizers which had been effective in reducing Nomex UV degradation should also be tried on E-11.

It was requested that copies of all previous monthly progress reports be sent to Dr. J. R. Emery of Dupont. Copies of reports number 1 through 9 were forwarded to Dr. Emery on May 28.

III. UV Degradation of Nomex Fabric.

Initial exposure studies have been carried out on Nomex fabric (Mil-C-38351, Type II, Class 1). This fabric is the one that will be used in the factorial experiment. Retention of breaking strength and elongation in the warp and fill directions are shown in Figures 1 and 2. In both carbon-arc and xenon-arc exposure the loss in breaking strength and elongation in the warp direction and the loss of breaking strength in the filling direction follow very similiar curves. The elongation in the filling direction decreases much more sharply. These experiments suggest that the 1" ravel strip test should be satisfactory for the proposed factorial experiment.

IV. Analytical Proceduces for Stabilizers

In order to study the effect of stabilizer concentration on UV stability it is necessary to be able to quantitavely determine the stabilizer concentration in Nomex fabric. It was decided that this could best be done by determining the concentration of stabilizer in

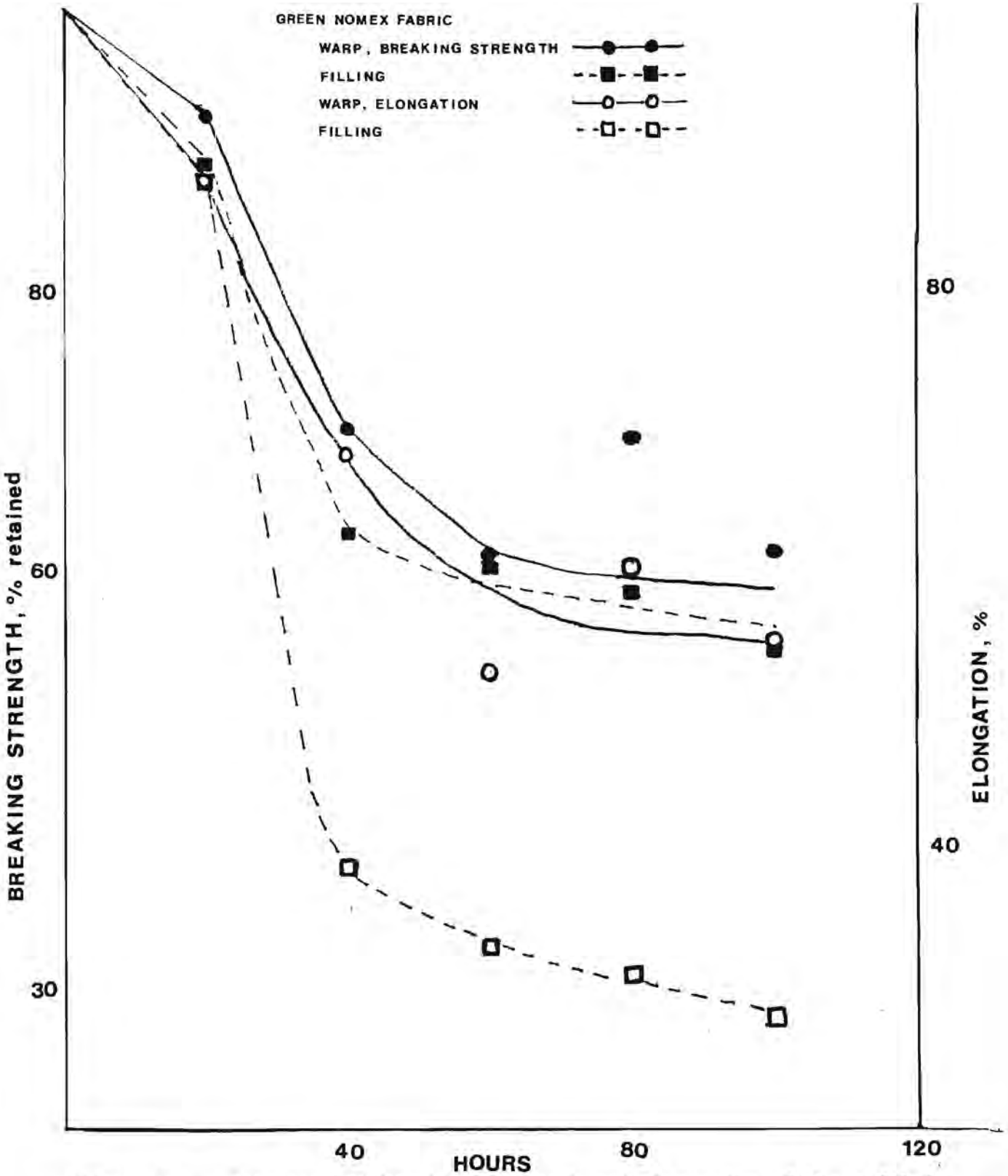


Figure 1 - - Retention of breaking strength and elongation of Nomex fibric exposure in the carbon-arc fadeometer.

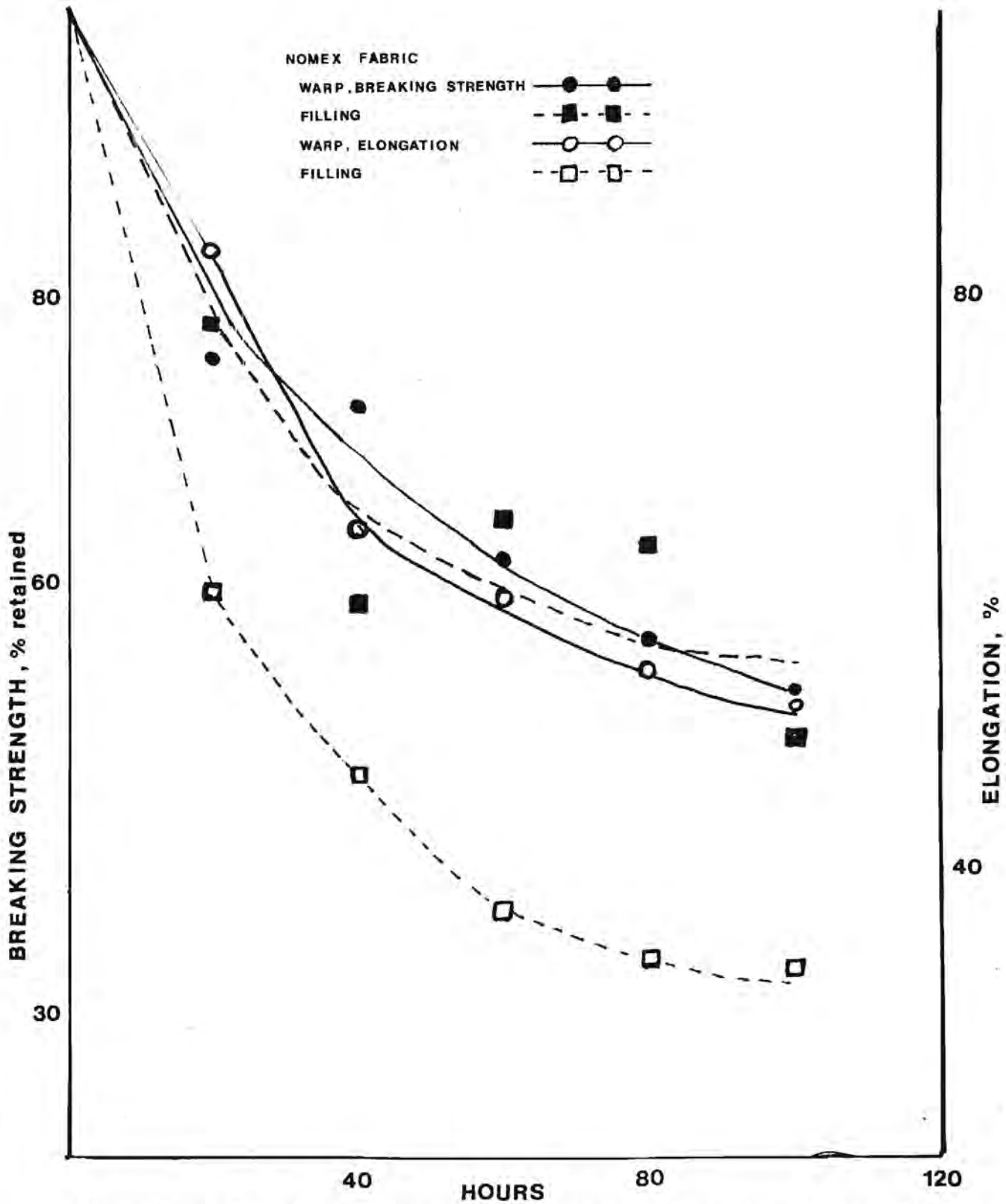


Figure 2 - - Retention of breaking strength and elongation of Nomex fabric exposed in the xenon-arc fadeometer.

the bath before and after treatment of the fabric samples and to determine the stabilizer concentration in the scouring baths. Concentration of stabilizers in the fabric can then be found by differences.

Fluorescence spectorcopy was selected for quantitative determination of the quantity of Blancophor AW in solution. The intense fluorescence of this material permits precise determination at very low concentrations. Standards were prepared in "dye bath" solutions and the analytical working curve shown in Figure 3 was obtained.

Absorption spectroscopy was used to establish the working curve for Tinuvin P shown in Figure 4.

Work is currently underway to develop an analytical procedure for oxanilide.

V. Stabilizers for E-11 Fabric

A small sample of E-11 Fabric has been obtained from Dupont. The quantities of fabric supplied are not sufficient for a complete testing program and Dupont is unable to supply a larger sample. Samples of E-11 fabric have been treated in "dyebaths" containing Tinuvin P and Blancophor AW. They will be exposed for 20 and 60 hours and the retention of elongation and breaking strength determined in the warp direction.

VI. Future Work

Studies on E-11 will be completed in the coming month and initial runs for the factorial experiment will begin.

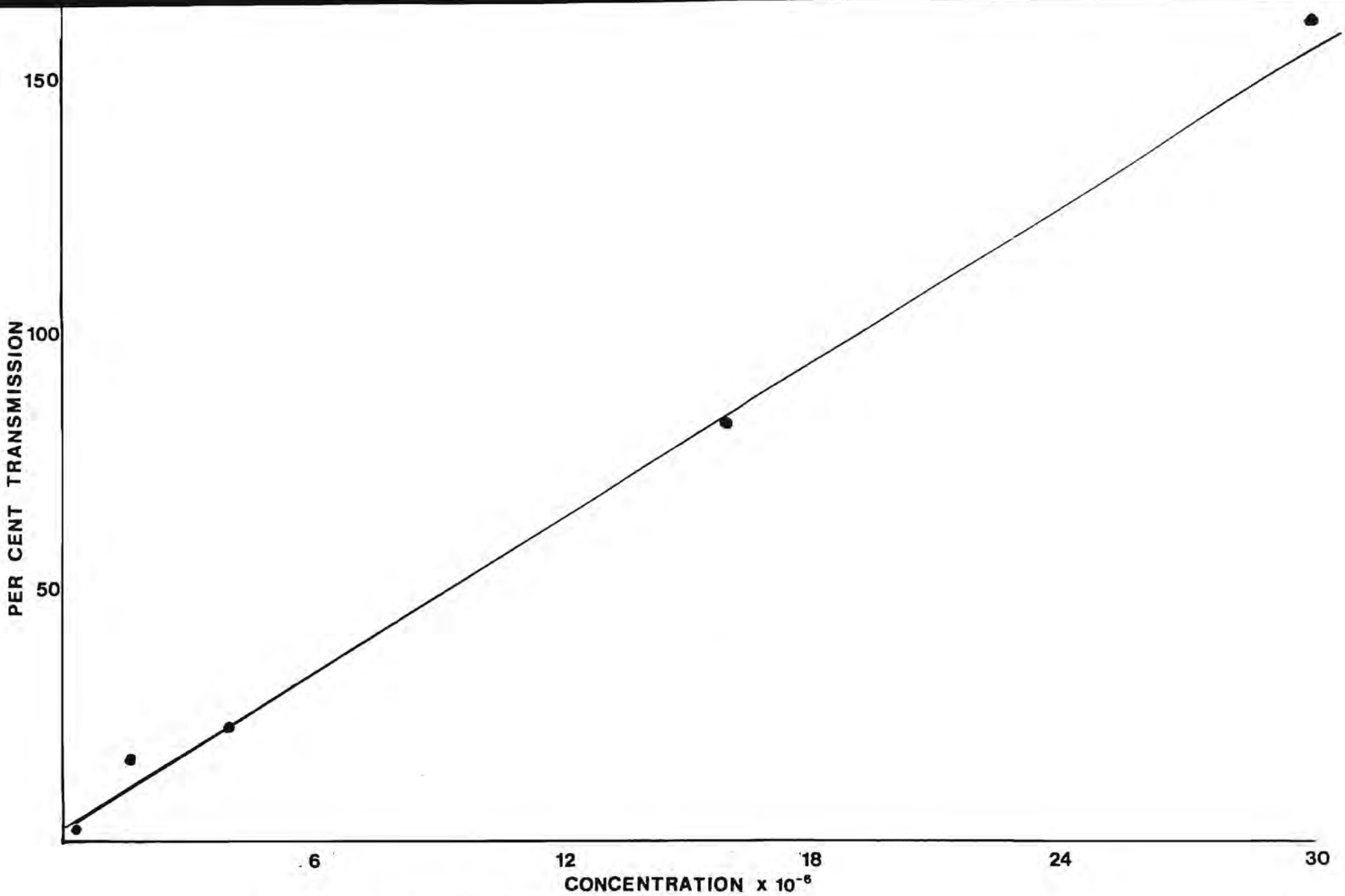


Figure 3 - - Analytical working curve for Blancophor AW.

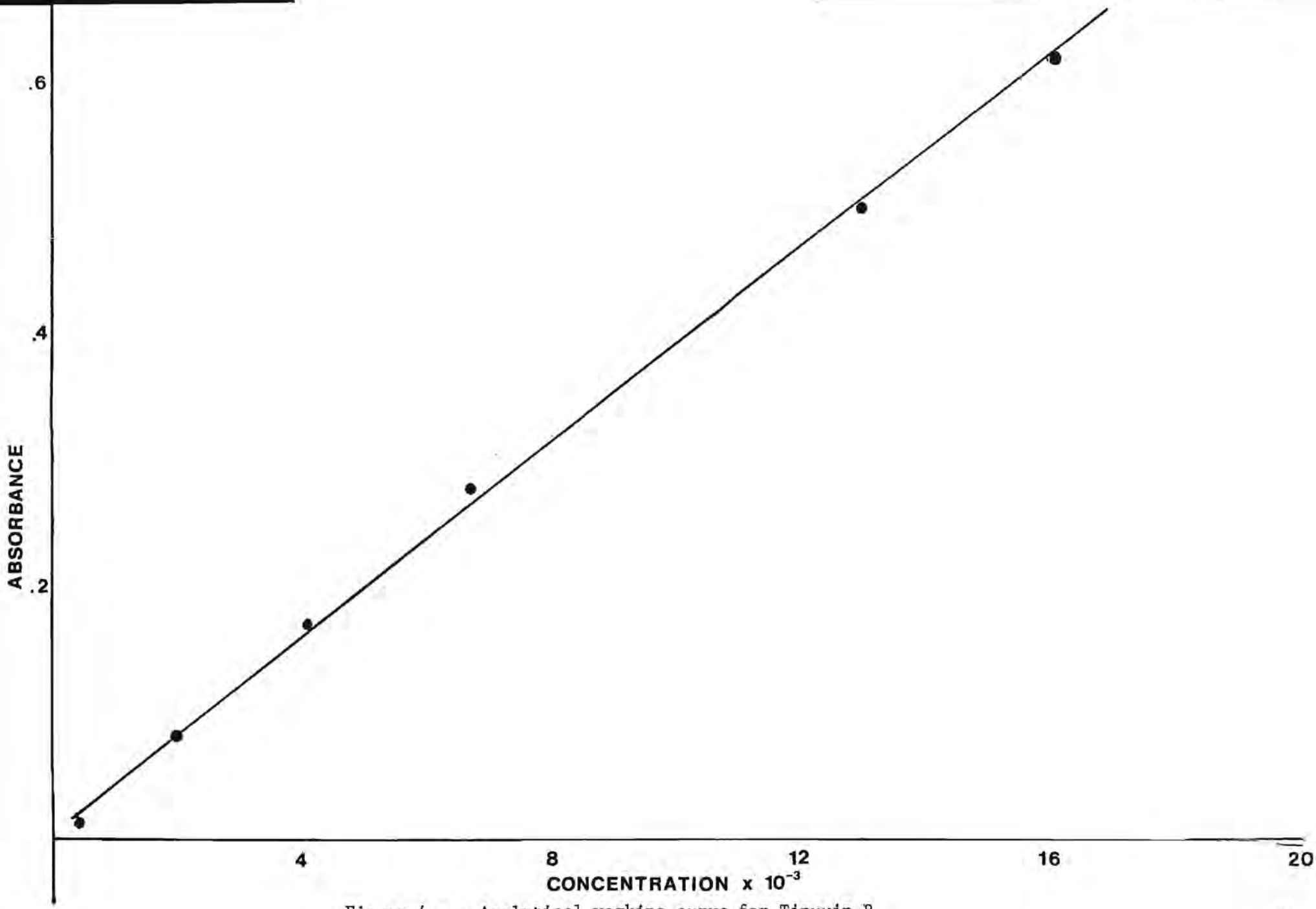
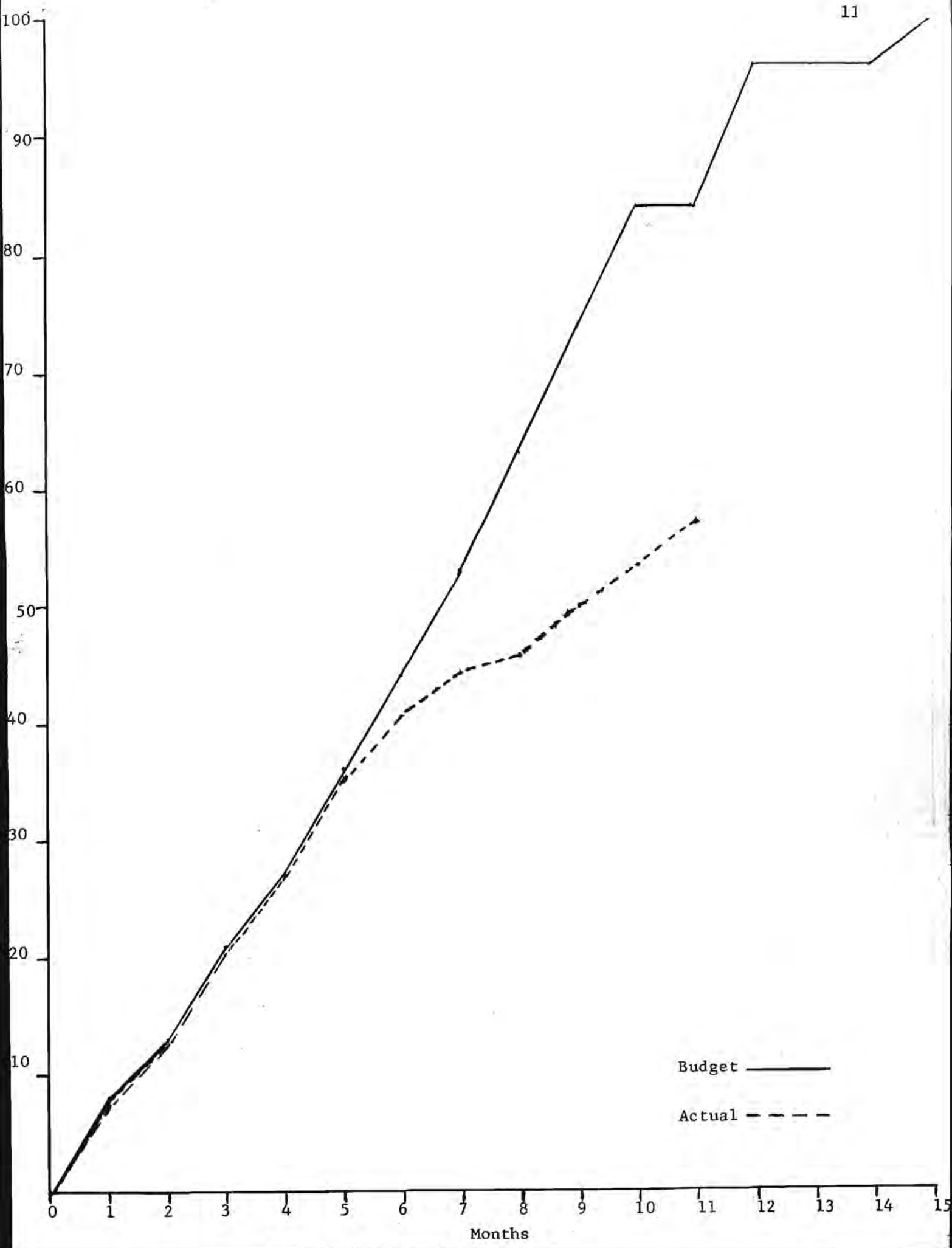


Figure 4 - - Analytical working curve for Tinuvin P.

VII. Budget

The funds budgeted and either expended or allocated for the first eleven months are shown on the attached graph.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E-27-623

Monthly Progress Report Number 12

(Mar. 26, 1975 - June 26, 1975)

Development of Ultraviolet Protection Nomex

Life Support SPO
Air Force Systems Command
Aeronautical Systems Division
Wright-Patterson Air Force Base, Ohio 45433

(Prepared Under Contract No. F33657-74-C-0716
by
Georgia Institute of Technology
Atlanta, Georgia 30332
W. C. Tincher, author)

Summary

Experiments on UV stability of experimental Nomex fabric E-11 have been completed. Results show that this material has UV degradation characteristics very similar to regular Nomex and can be stabilized by the same additives found to be effective in regular Nomex.

The factorial experiment for development of a stabilizer system for Nomex is nearing completion. Eight of the eleven samples have been exposed and are being tested.

Several new experimental stabilizers have been obtained from a leading manufacturer of UV stabilizers. These materials are being tested for effectiveness in Nomex.

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this month has been directed toward completion of the
nt for selection of UV stabilizer systems for Nomex.
been conducted on E-11 type Nomex and several new
tes have been obtained and are being screened for
improving Nomex UV stability.

lizer Systems

nt stabilizers (Blancophor AW, Tinuvin P, and Oxanilide)
ated at 4 concentration levels (0,33,66 and 100% OWF)
n fabric (Mil-C-38351, Type II, Class 1) to establish
ions for stabilization and to determine if synergistic
t. Samples are being exposed for periods of 0,20,40,60
tested by the 1" ravel strip method in the warp direction.
iments is shown in Table 1. Exposures have been completed
through 8. Equipment problems with the carbon-arc fade-
ted completion of the exposures. They will be completed
ive delivery of a transformer for the fadeometer.

11 Nomex Fabric

e experimental E-11 (which is considered for replacement
yarn applications) Nomex fabrics have been treated in
ing Tinuvin P and Blancophor AW. The treated fabrics have
0 and 60 hours in the carbon-arc fadeometer and the
aking strength determined in the warp direction by the

Table 1

Factorial For Selection of Stabilizer Systems

Experiment No.	Sample*
1	$A_3B_1C_1$
2	$A_3B_1C_3$
3	$A_2B_2C_2$
4	$A_2B_2C_2$
5	$A_1B_3C_1$
6	$A_1B_1C_1$
7	$A_3B_3C_1$
8	$A_1B_3C_3$
9	$A_3B_3C_3$
10	$A_1B_1C_3$
11	$A_0B_0C_0$

* A = Blancophor AW

B = Tinuvin P

C = Oxanilide

0 = 0 % OWF

1 = $33\frac{1}{3}$ % OWF

2 = $66\frac{2}{3}$ % OWF

3 = 100 % OWF

1" ravel strip method. Results are shown in Figures 1 and 2 where per cent retention of breaking strength and elongation are compared for treated and blank dyed samples. These results clearly indicate that systems which stabilize regular Nomex are also effective on E-11 fabrics. The results are consistent with the proposed structure of E-11 yarn (a fiber blend of predominantly regular Nomex with a small quantity of a more thermally stable fiber).

IV. Additional Stabilizer Candidates for Nomex

As information on other possible stabilizers becomes available, these new materials are being screened for effectiveness in stabilizing Nomex. A discussion of preliminary results of screening experiments with representatives of Ciba-Geigy has led to the suggestion of 5 other possible stabilizers for Nomex (Irganox MD1024, Uvitex B, Tinopol SFG, Tinopol CBS and GI 09-367) including some experimental materials under development in the Ciba-Geigy laboratories. Results for these stabilizer candidates will be reported next month.

V. Future Work

The factorial experiments and screening studies on other UV stabilizer candidates will be completed in the coming month.

VI. Budget

The funds budgeted and either expended or allocated for the first twelve months are shown on the attached graph.

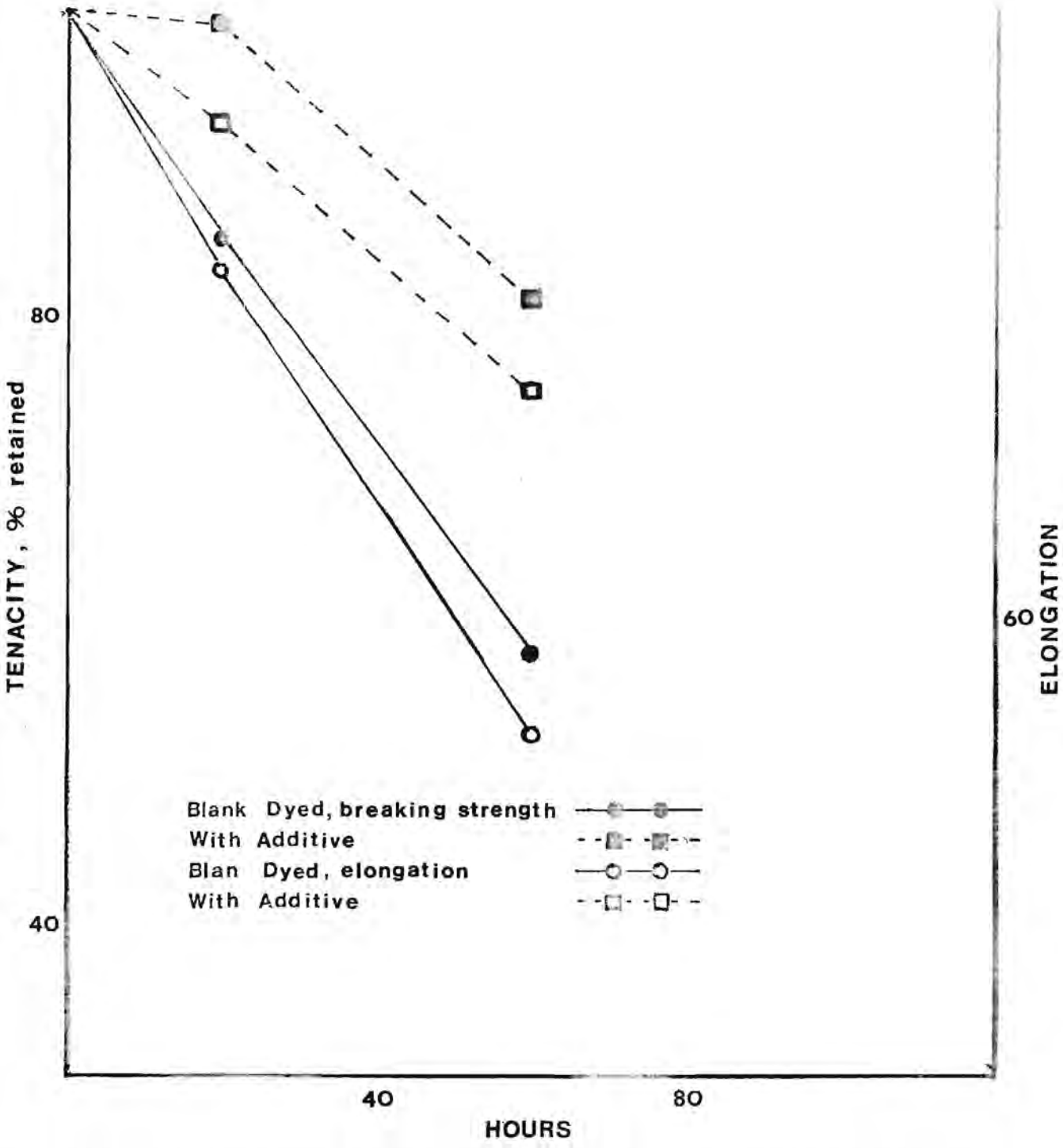


Figure 1-- Retention of elongation and breaking strength for E-11 Nomex fabric containing Tinuvin P compared to blank dyed fabric.

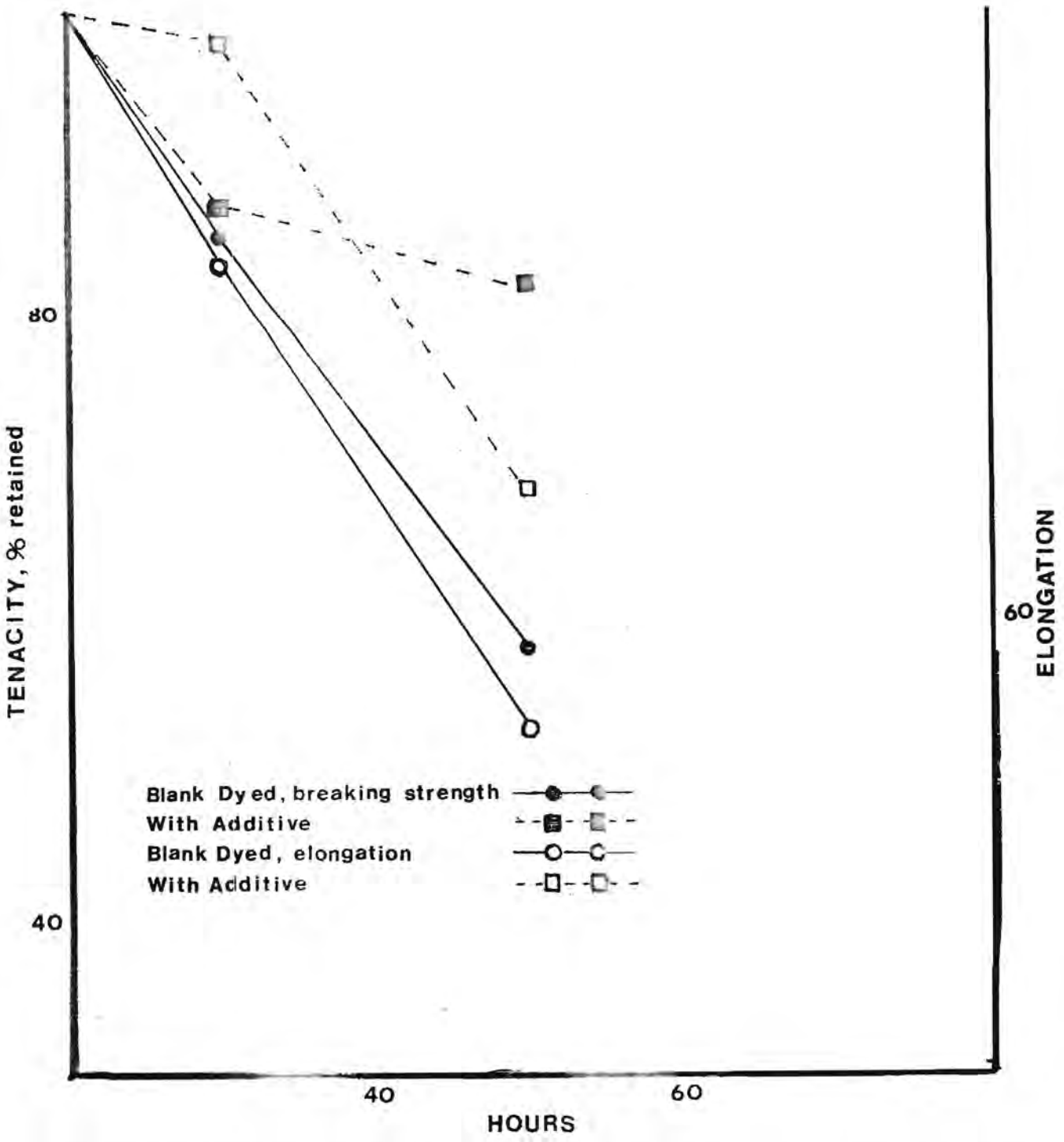
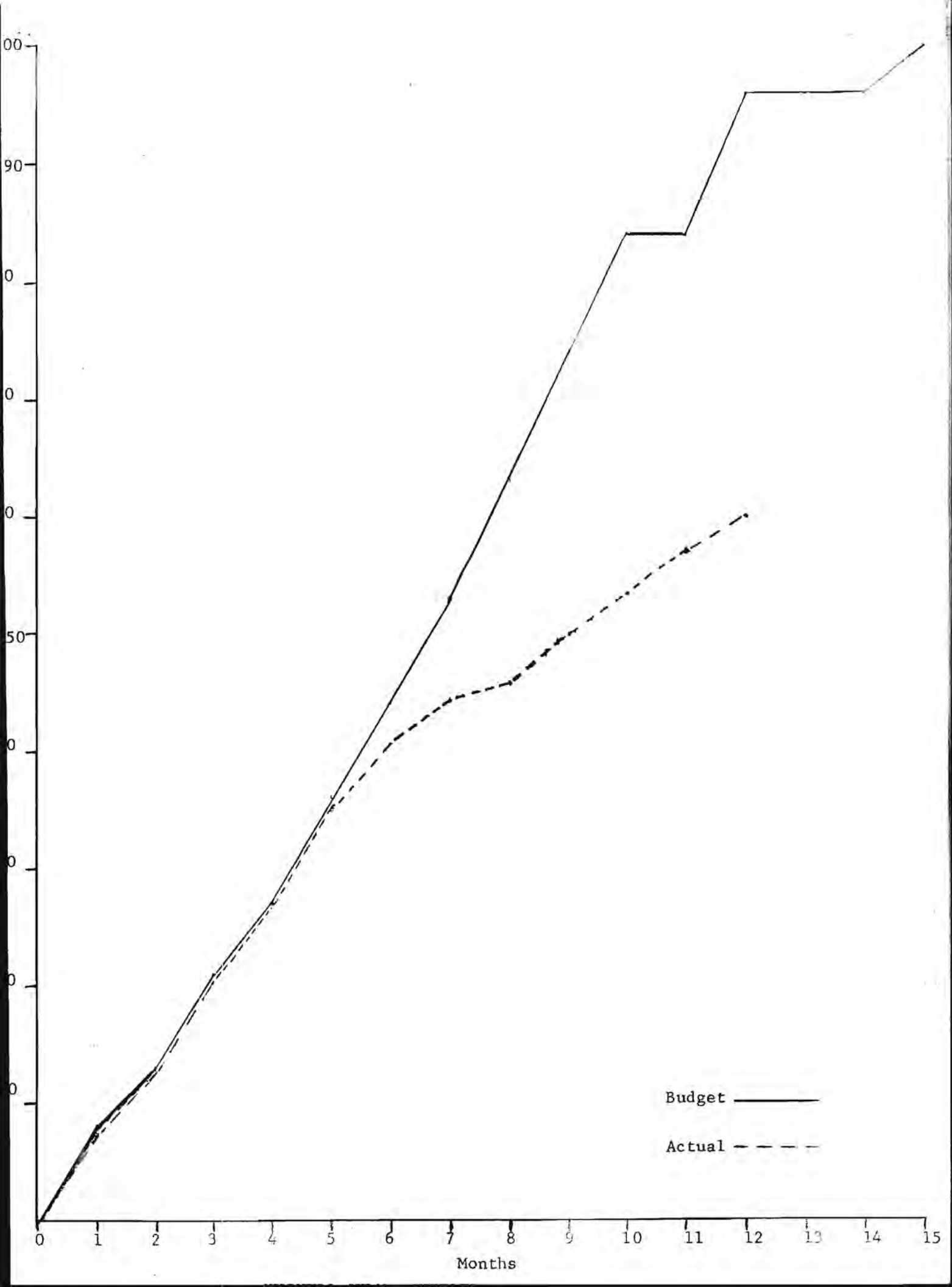


Figure 2-- Retention of elongation and breaking strength for E-11 Nomex fabric containing Blancophor AW compared to blank dyed fabric.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E-27-623

Monthly Progress Report Number 13

(June 26, 1975 - July 26, 1975)

Development of Ultraviolet Protection Nomex

Life Support SPO
Air Force Systems Command
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Wright-Patterson Air Force Base, Ohio 45433

(Prepared Under Contract No. F33657-74-C-0716)
by
Georgia Institute of Technology
Atlanta, Georgia 30332
W. C. Tincher, author)

Summary

The factorial experiment for development of a stabilizer system for Nomex has been completed and the results analyzed. A favorable synergistic effect has been observed between two of the stabilizers, Tinuvin P and Oxanilide. Combinations of these two stabilizers are recommended for study in Phase II of the project.

Blancophor AW was not as effective in providing UV protection for Nomex as the initial screening experiments had suggested. This stabilizer also had an adverse affect on the dye lightfastness of sage green Nomex fabric.

A meeting to discuss results of the factorial experiment and to review plans for Phase II of the project is scheduled for August 28.

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I. Introduction

Major effort this month has been directed toward completion of the factorial experiment for selection of UV stabilizer systems for Nomex. Three different stabilizers (Blancophor AW, Tinuvin P, and Oxanilide) were investigated at 4 concentration levels (0,33,66, and 100% OWF) on Nomex sage green fabric (MIL-C-38351, Type II Class 1). Samples were exposed for periods of 0,20,40,60,80, and 100 hours and tested by the 1" ravel strip method in the warp direction. Order of the experiments is reviewed in Table 1.

II. Analysis of the Factorial Experiment

Results of breaking strength tests from specimens treated with the three UV inhibitors and irradiated at levels up to 100 hours in the fadeometer were analyzed to determine statistical significance. Experimental samples were prepared in treatment combinations of the three UV inhibitors as shown in Table 1. Briefly, these samples included treatment combinations of the three inhibitors at three levels of concentrations. The effects of intermediate levels of the inhibitors were determined only in a treatment combination at which all of the inhibitors were at the intermediate level. All other treatment combinations were made up from addition of the three inhibitors at their low and high concentrations. One sample was prepared in which all materials were present except for the UV inhibitors. This sample provides information on strength loss associated with the processing conditions involved in the preparation of the samples.

A measure of the random variation associated with base fabric variability, application of inhibitors, degradation by UV irradiation, and testing of the specimens was obtained from replications made on the treatment combination in which inhibitors were added at their intermediate level. This variation

Table 1

Factorial For Selection of Stabilizer Systems

Experiment No.	Sample*
1	$A_3B_1C_1$
2	$A_3B_1C_3$
3	$A_2B_2C_2$
4	$A_2B_2C_2$
5	$A_1B_3C_1$
6	$A_1B_1C_1$
7	$A_3B_3C_1$
8	$A_1B_3C_3$
9	$A_3B_3C_3$
10	$A_1B_1C_3$
11	$A_0B_0C_0$

* A = Blancophor AW

B = Tinuvin P

C = Oxanilide

0 = 0 % OWF

1 = $33\frac{1}{3}$ % OWF

2 = $66\frac{2}{3}$ % OWF

3 = 100 % OWF

was calculated by an analysis of variance technique. It is assumed that the random variation measured in this treatment combination is the same as that involved in all other treatment combinations.

The main effects and interactions of the three UV inhibitors was determined by analyzing the data as a 2^3 factorial experiment in which three factors - the three UV inhibitors - were varied at two levels. The two levels used, of course, were the low and high concentrations at which the UV inhibitors were added. The statistical significance of these effects was determined by comparing the variances associated with the main effects and interactions to the measure of random variation calculated as described above.

The results of this analysis are shown in Table II. Prior to exposure to UV irradiation, it appears that two main effects - the addition of Blancophor AW and Oxanilide - are statistically significant; that is, strength of samples prepared from these two inhibitors is affected by the concentration of these inhibitors. The nature of this effect for each inhibitor can be seen in Figures 1 and 3, both of which show that breaking strength decreased as concentration of the UV inhibitor increased. The interaction effect of concentration level and combination of Blancophor AW and Oxanilide prior to UV exposure was also statistically significant as was the third order interaction involving all three UV inhibitors. The nature of the interaction between Blancophor AW and Oxanilide can be seen in Figure 4, which shows clearly that the presence of either inhibitor at the higher concentration results in significant strength losses. Variation in the third order interaction, although statically significant, is probably attributable to random variations.

Continued analysis of Table II shows principally that the effect of differences in level of Tinuvin P are most pronounced at all levels of UV

Table II, F-Ratios for 2^3 Factorial Experiment

Source of Variation	0	20	40	60	80	100
A	20.3	9.3	6.0	101.7	11.2	1.7
B	3.1	62.6	23.8	101.3	28.1	0.1
C	6.0	1.4	6.5	10.1	0.3	1.9
AB	0.3	1.0	1.0	16.3	8.6	1.7
AC	11.6	11.5	1.3	0.1	1.7	0.0
BC	3.0	10.4	9.3	0.8	9.0	0.1
ABC	4.5	1.8	0.3	0.0	0.0	19.9

A - Blancophor AW

B - Tinuvin P

C - Oxanilide

AB, AC, BC, ABC represent the combined effects of the three UV inhibitors

Value of F-ratio significant at 95 percent probability oevel is 3.8; at 99 percent probability level, F is 6.6.

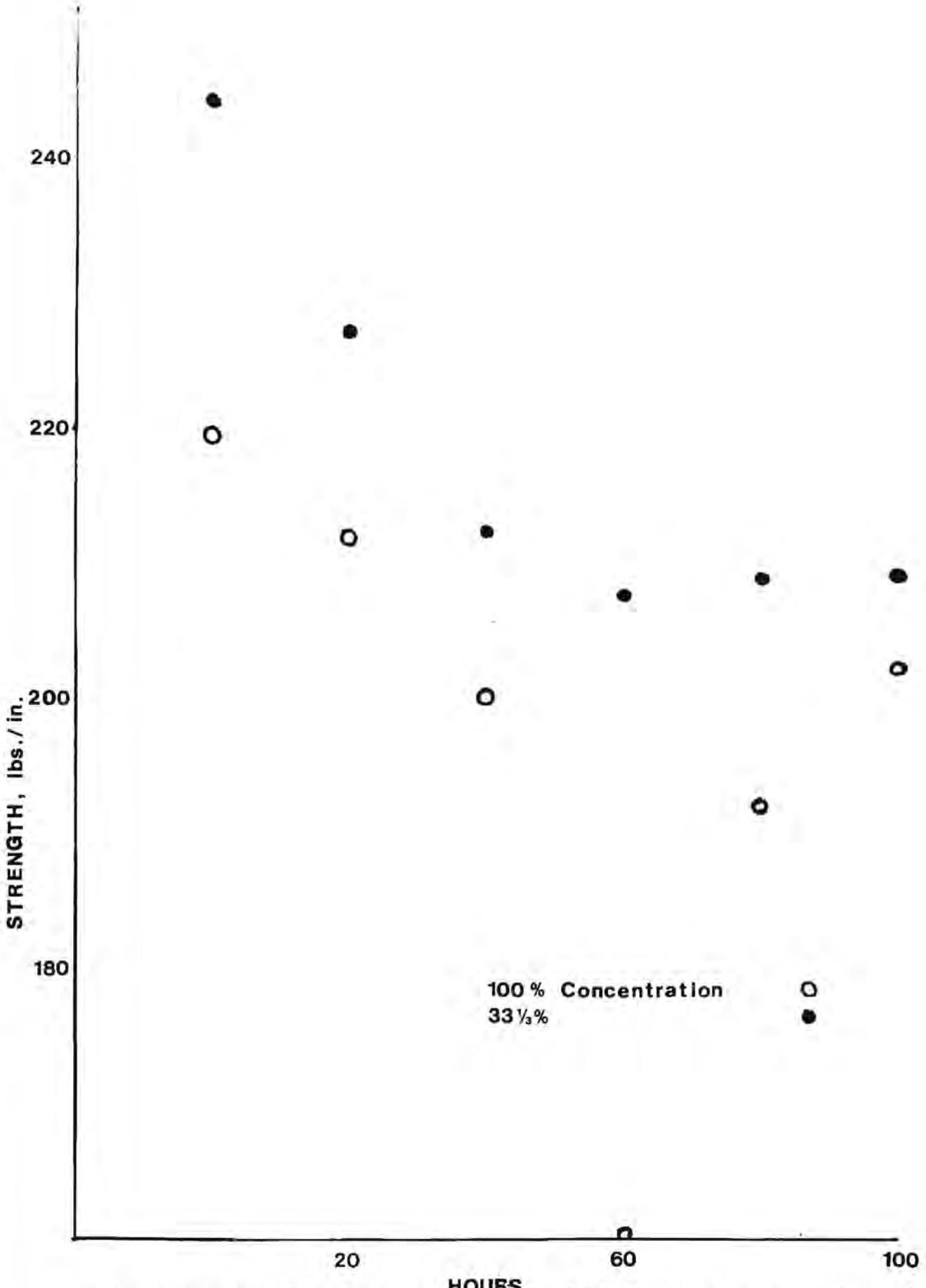


Figure 1-- The effects of concentration of Blancophor AW on resistance to strength loss from UV irradiation.

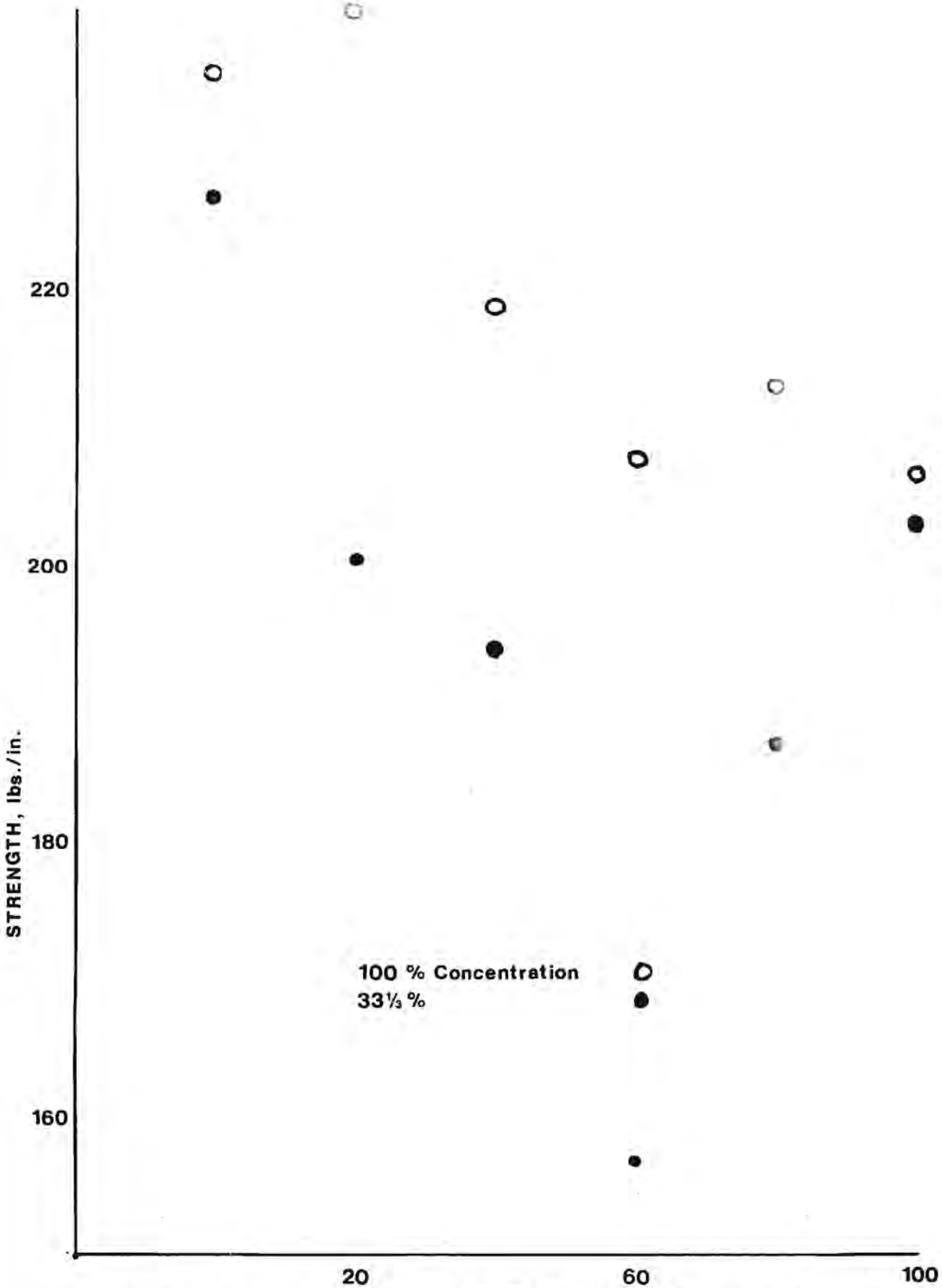


Figure 2— The effects of concentration of Tinuvin P on resistance to strength loss from UV irradiation

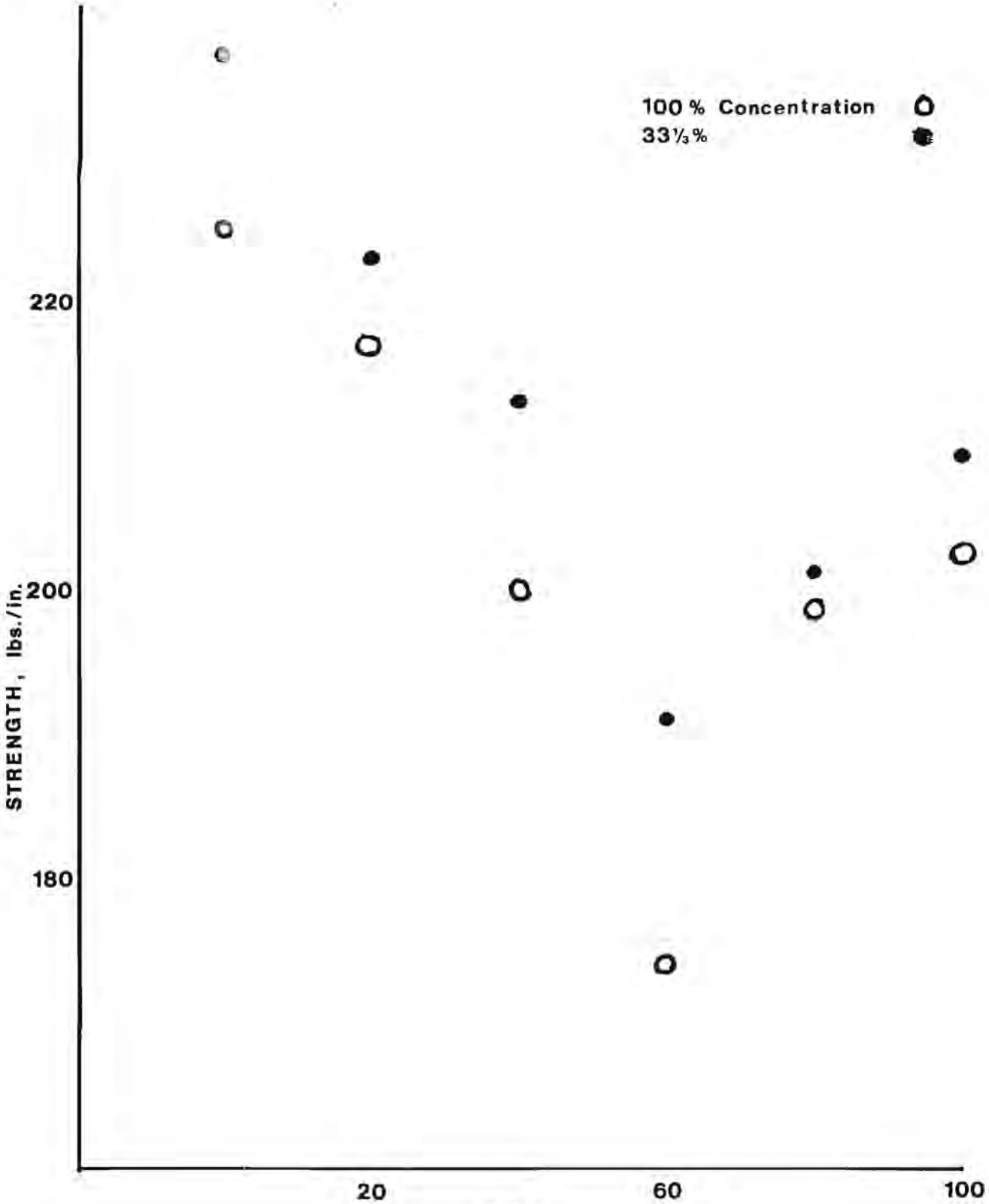


Figure 3-- The effects of concnetration of Oxanilide on resistance to strength loss from UV irradiation

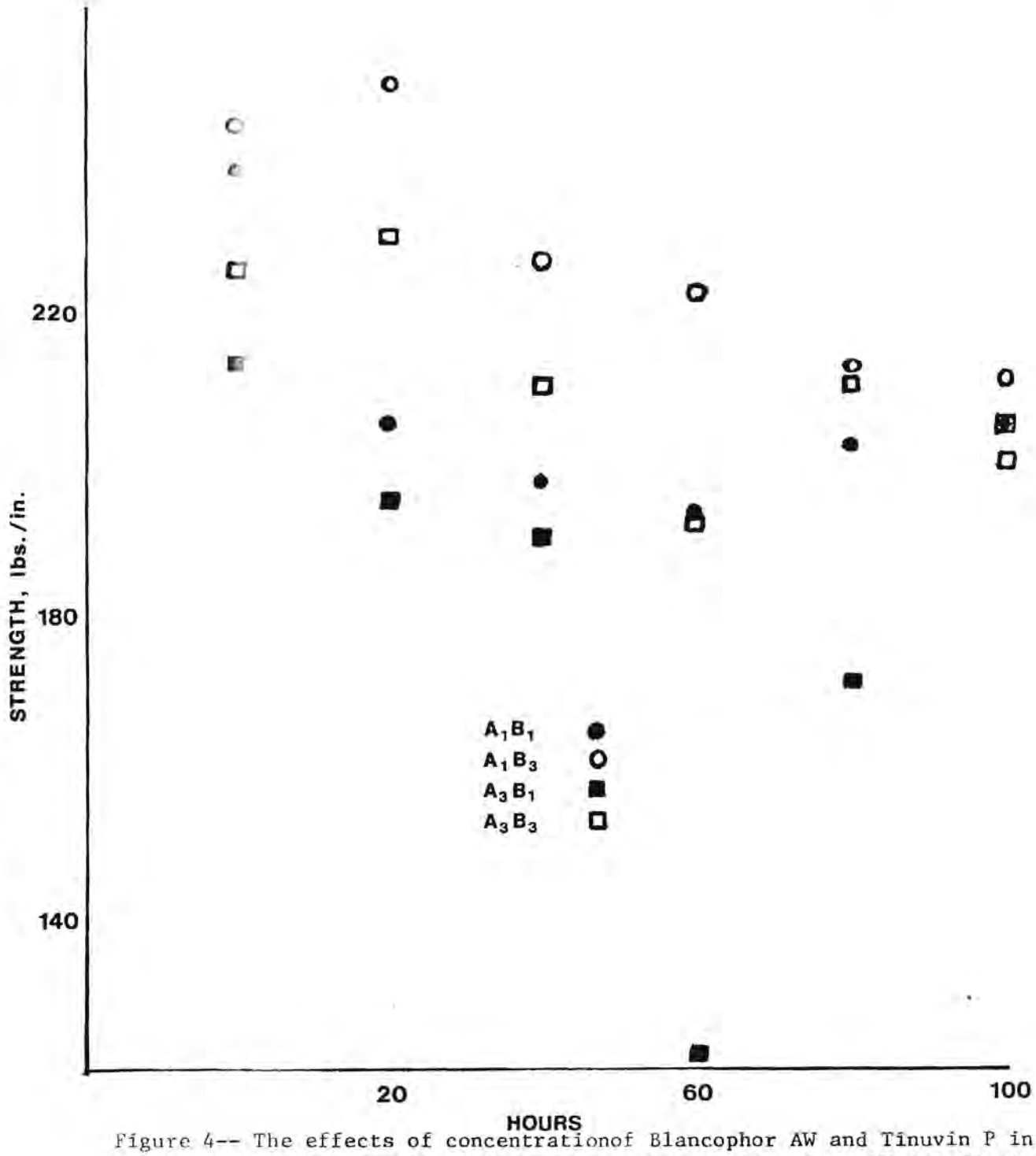


Figure 4-- The effects of concentrationof Blancophor AW and Tinuvin P in combination on resistance to strength loss from UV irradiation.

exposure up to 100 hours. Examination of Figure 2 shows that strength is improved as concentration level of Tinuvin P is increased. It is also important to note from Table II that none of the main effects and interactions are significant at 100 hours exposure, indicating the loss of any effectiveness of the additives at that level of irradiation.

Examination of all the Figures shows that anomalous results were obtained at the 60-hour exposure level for several samples. These unusually low results are probably attributable to errors in strength measurement as opposed to unusual effects of UV irradition or sample preparation. Detrimental effects of UV irradiation would be seen in very low strength values of samples at 80 and 100 hours.

The average strength measured for each treatment combination and exposure level is shown in Table III. From this Table, it is apparent that the highest strengths were obtained at all levels of UV exposure from the treatment combination in which Blancophor AW and Oxanilide were at low concentration levels and Tinuvin P was at its high level. Other beneficial combinations appear to be the combination of all three inhibitors such that Tinuvin P is included at high concentration. It should be noted that the 95 percent confidence limit on the averages shown in the Table is $\pm$ 14 pounds, based on the random variation calculated in the manner discussed previously.

An effect completely different from all of the others is seen in the treatment combination in which all three UV inhibitors were included at the intermediate concentration. No loss in strength was observed as UV exposure increased. At present, there is no explanation for this finding.

The percent retention of breaking strength and elongation for each of

Table III. Average Strength Measured at Various UV Exposure Levels for All Treatment Combinations

Treat. Comb.	Average Strength at Fadeometer Hours					
	0	20	40	60	80	100
$A_oB_oC_o$	224	198	170	160	159	146
$A_1B_1C_1$	244	219	213	199	199	197
$A_1B_1C_3$	234	192	182	186	206	213
$A_1B_3C_3$	221	240	224	212	201	198
$A_3B_1C_1$	212	184	203	127	162	218
$A_3B_1C_3$	215	206	178	117	180	191
$A_3B_3C_3$	229	230	215	183	207	207
$A_1B_3C_1$	270	260	230	233	227	229
$A_3B_3C_1$	222	229	205	202	217	193
$A_2B_2C_2$	203	217	218	219	220	221

95% Confidence Limit = $\pm$ 14 lbs.

$A_oB_oC_o$ - UV inhibitors not present

$A_1B_1C_1$ - UV inhibitors present in lowest concentrations

$A_3B_3C_3$ - UV inhibitors present in highest concentrations

the fabrics in the factorial study are shown in Figures 5-14. With the exception of the 60 hour exposures for samples $A_3B_1C_1$ and $A_3B_1C_3$ results are reasonably consistent.

III. Recommendations for Phase II

Based on results of the factorial experiment the following systems are suggested for further study:

1. A, B, and C at equal concentration levels
2. B and C in a 3 to 1 ratio
3. B alone at two levels.

It would be very desirable in terms of other properties to be able to reduce the level of UV stabilizers to as low a concentration as is consistent with good stability. Selected experiments are now underway to better identify appropriate levels of addition for the Phase II experiment.

IV. Future Work

Fabrics containing additives at 1 and 10% each have been prepared and are now under test. A meeting is scheduled for August 28 to review plans for Phase II.

V. Budget

The funds budgeted and either expended or allocated for the first thirteen months are shown on the attached graph.

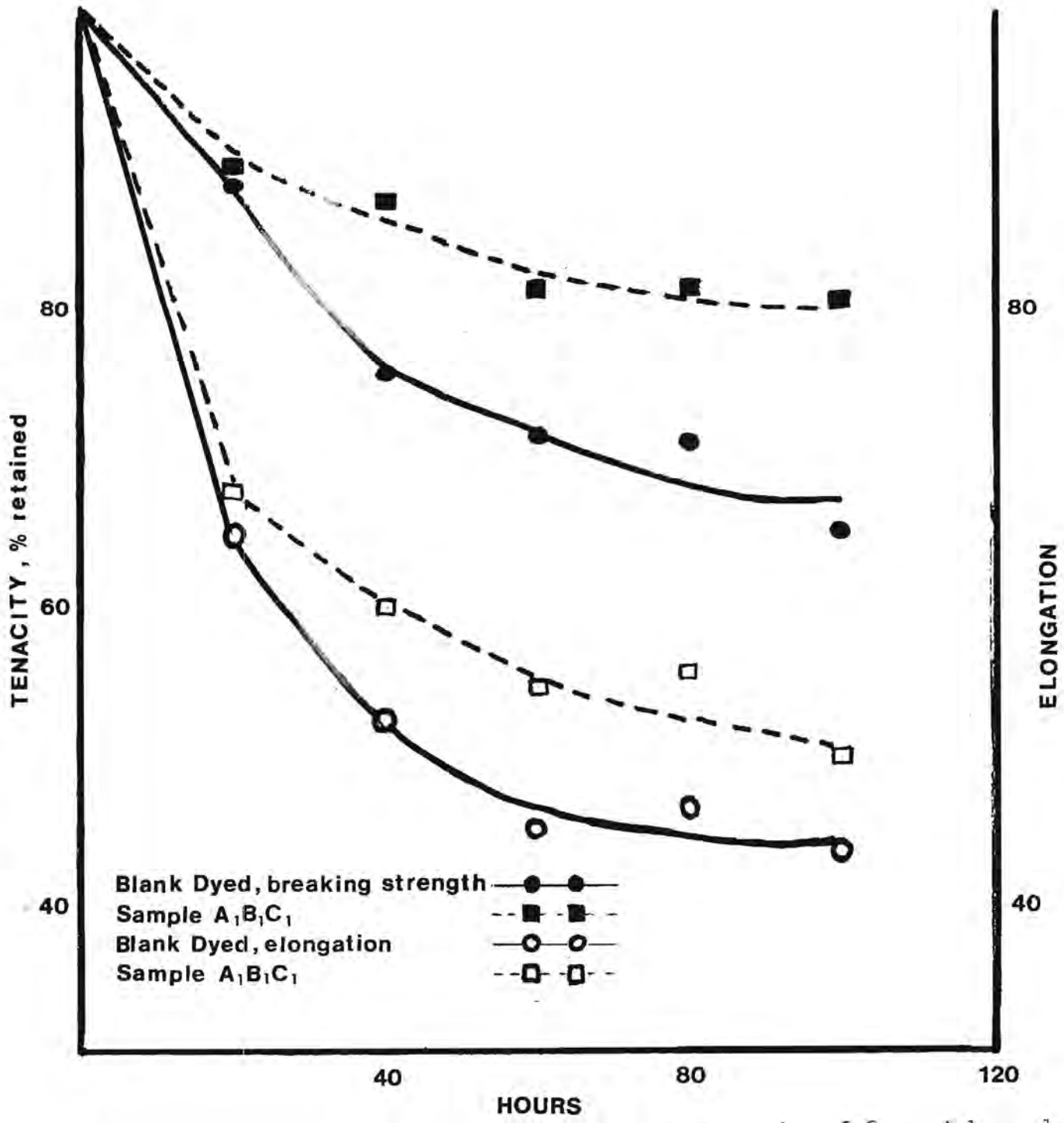


Figure 5-- Retention of breaking strength and elongation of factorial sample $A_1 B_1 C_1$ compared to control ($A_0 B_0 C_0$) on exposure to the carbon-arc fadeometer.

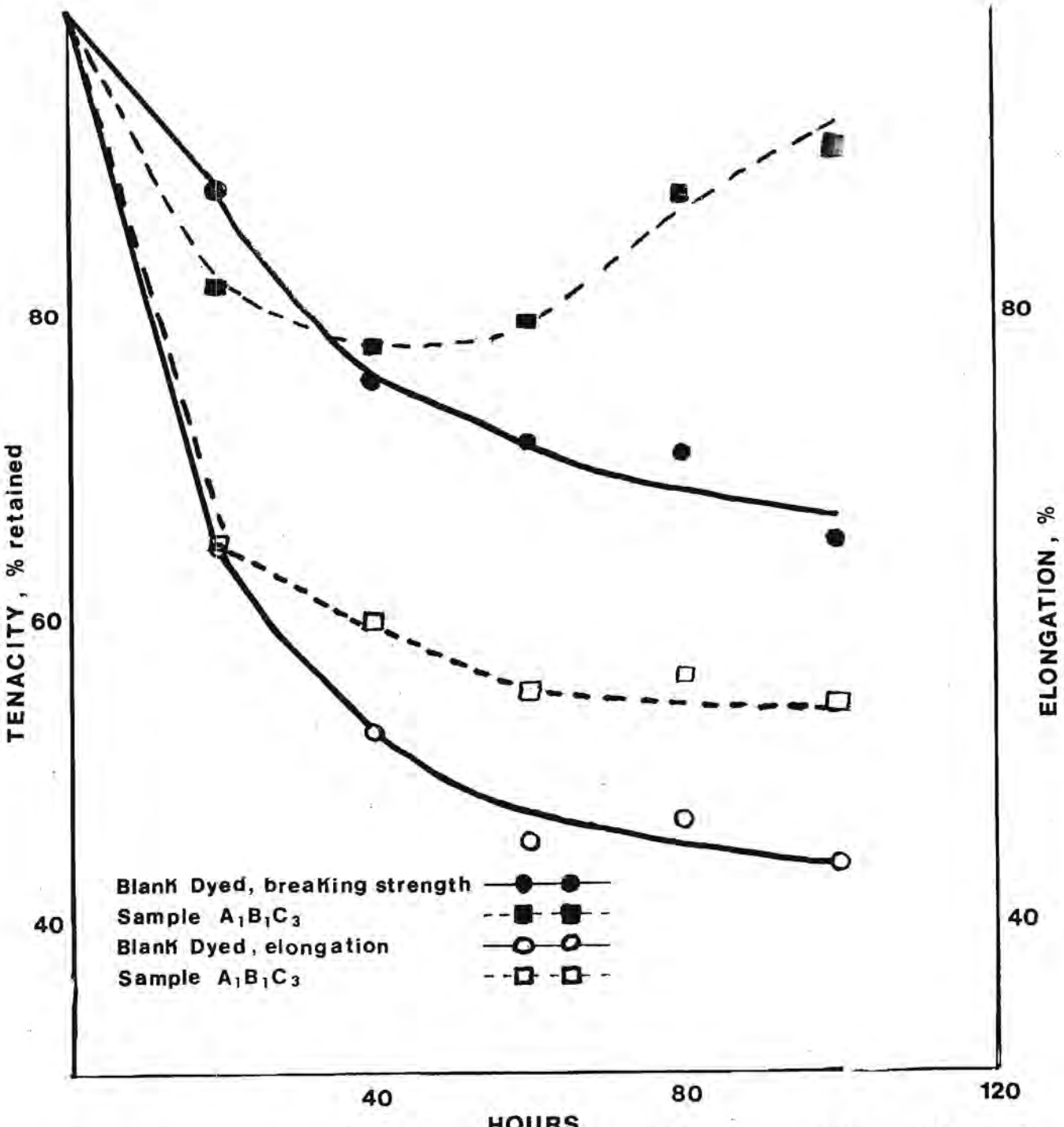


Figure 6-- Retention of breaking strength and elongation of factorial sample $A_1B_1C_3$ compared to control ($A_oB_oC_o$) on exposure to the carbon-arc fadeometer

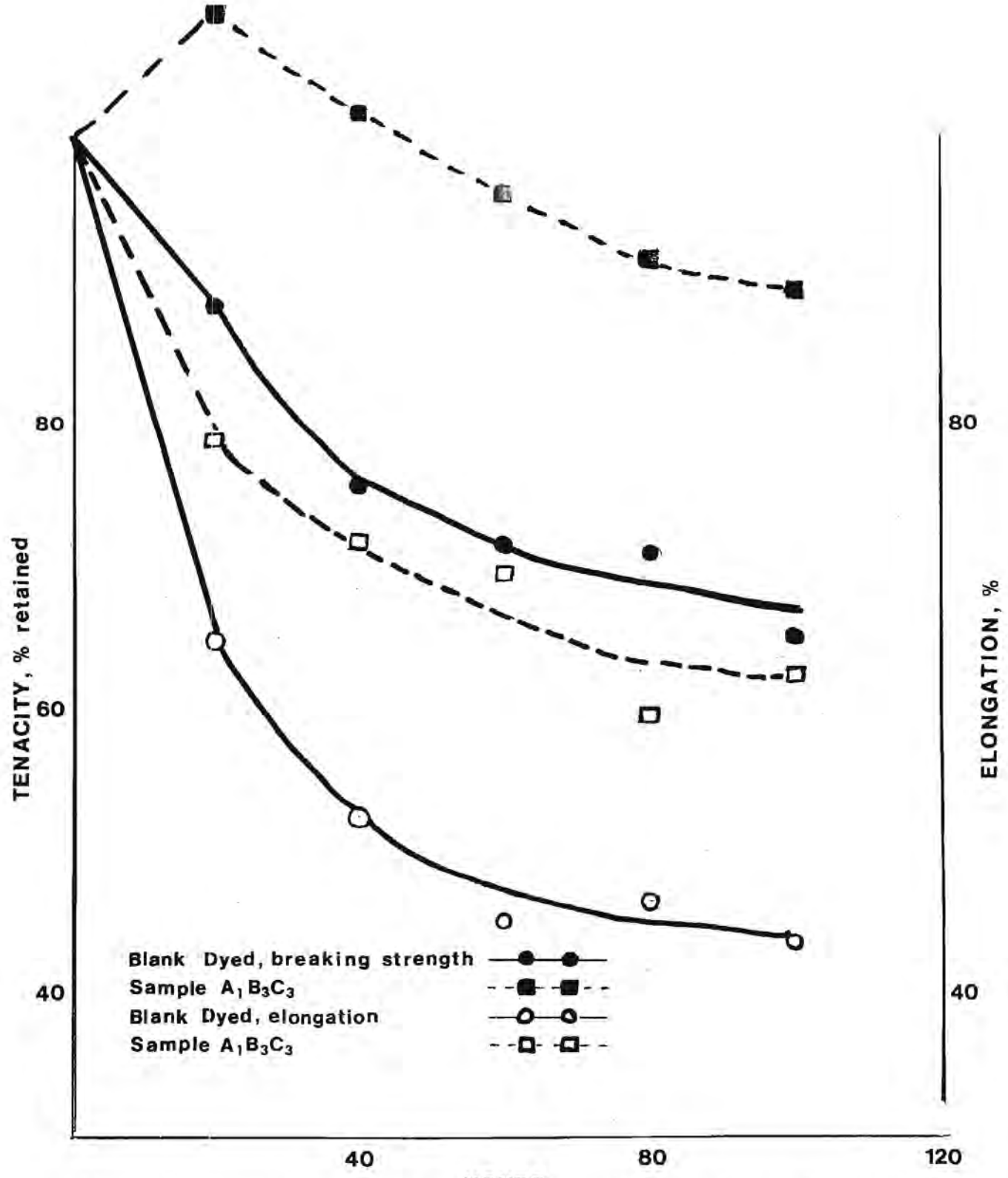


Figure 7-- Retention of breaking strength and elongation of factorial sample $A_1B_3C_3$ compared to control ($A_oB_oC_o$) on exposure to the carbon-arc fadeometer

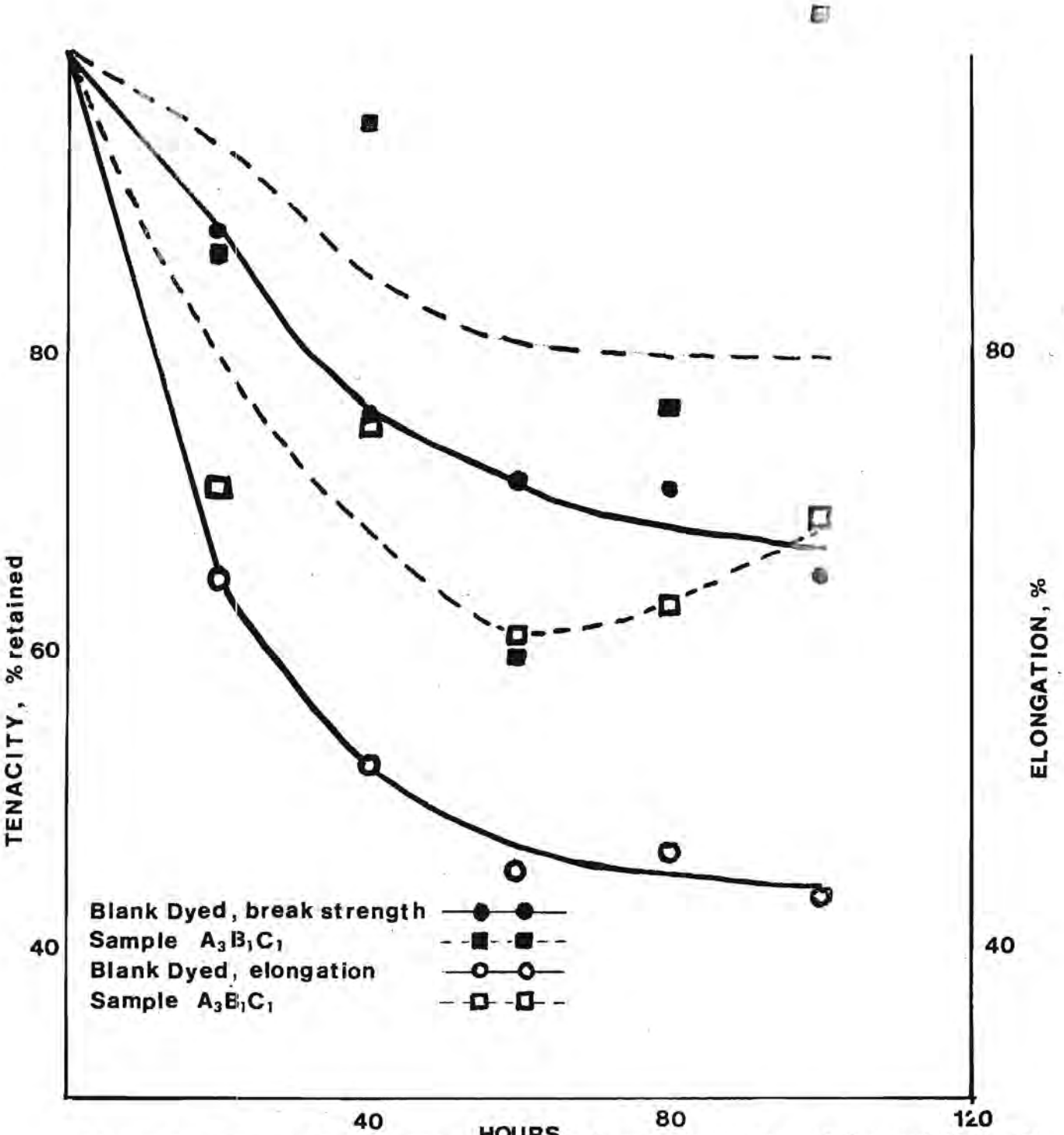


Figure 8-- Rentention of breaking strength and elongation of factorial sample $A_3B_1C_1$ compared to control ($A_oB_oC_o$) on exposure to the carbon-arc fadeometer

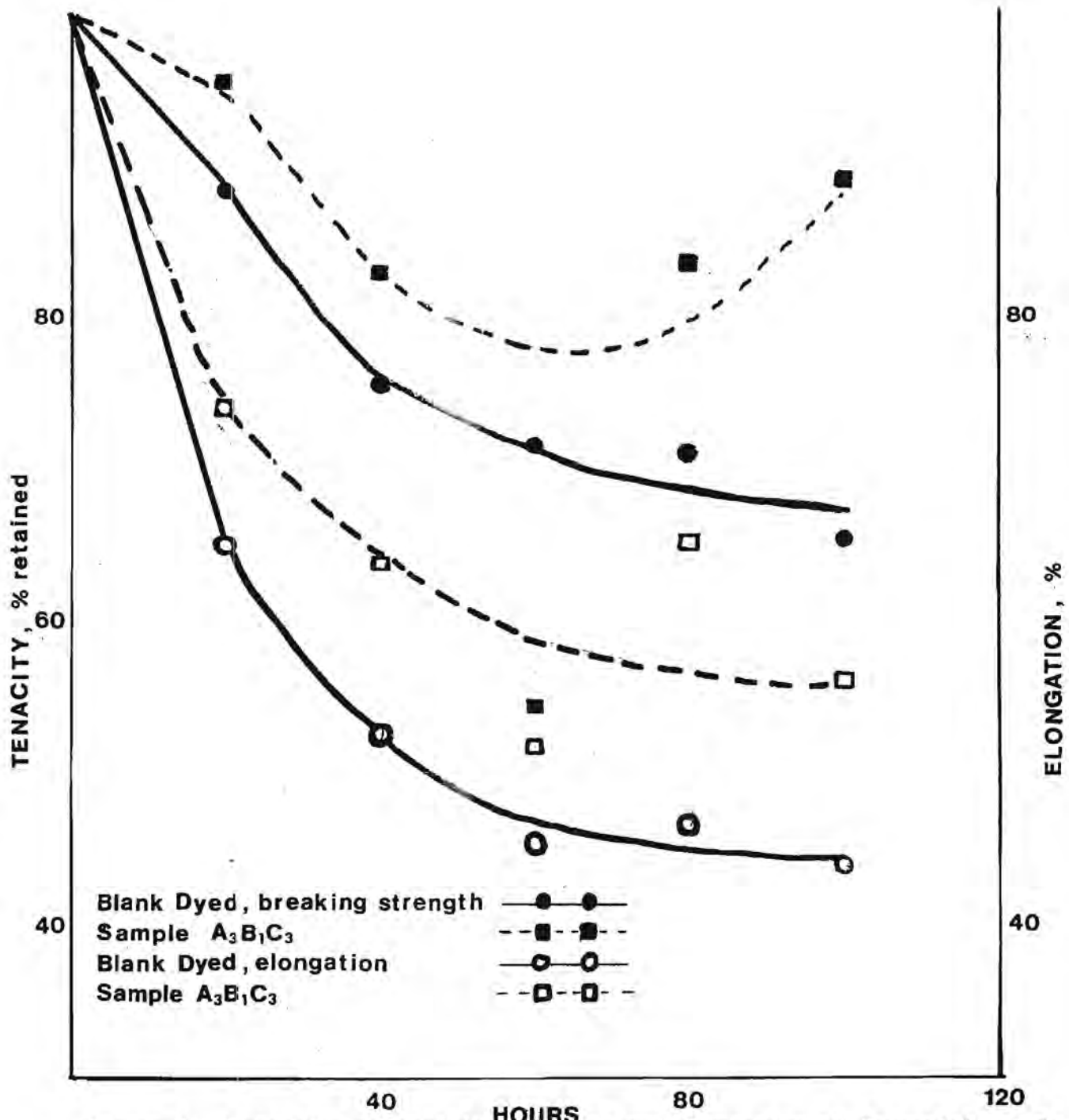


Figure 9-- Retention of breaking strength and elongation of factorial sample $A_3B_1C_3$ compared to control ($A_oB_oC_o$) on exposure to the carbon-arc fadeometer

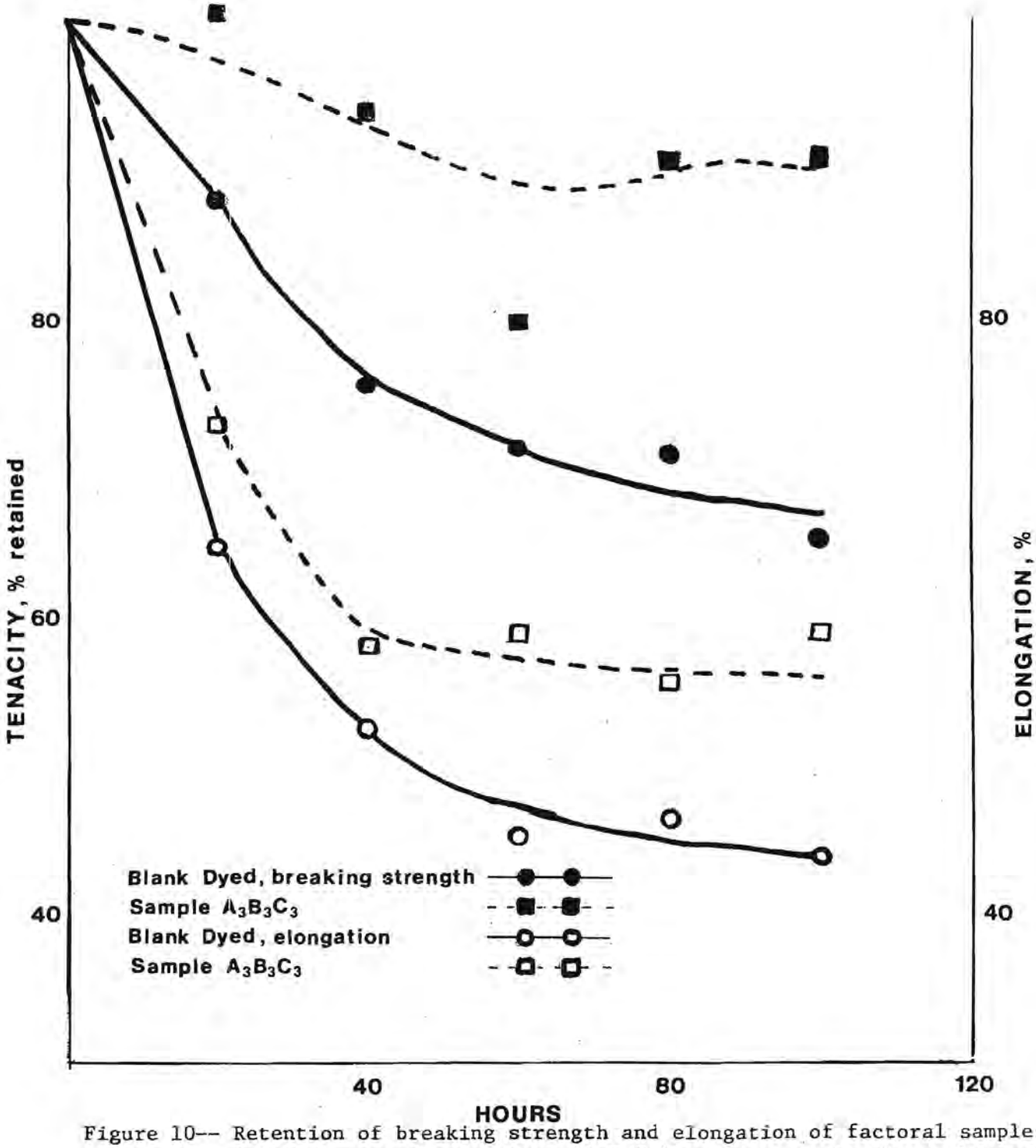


Figure 10-- Retention of breaking strength and elongation of factoral sample $A_3B_3C_3$ compared to control ($A_oB_oC_o$) on exposure to the carbon-arc fadeometer

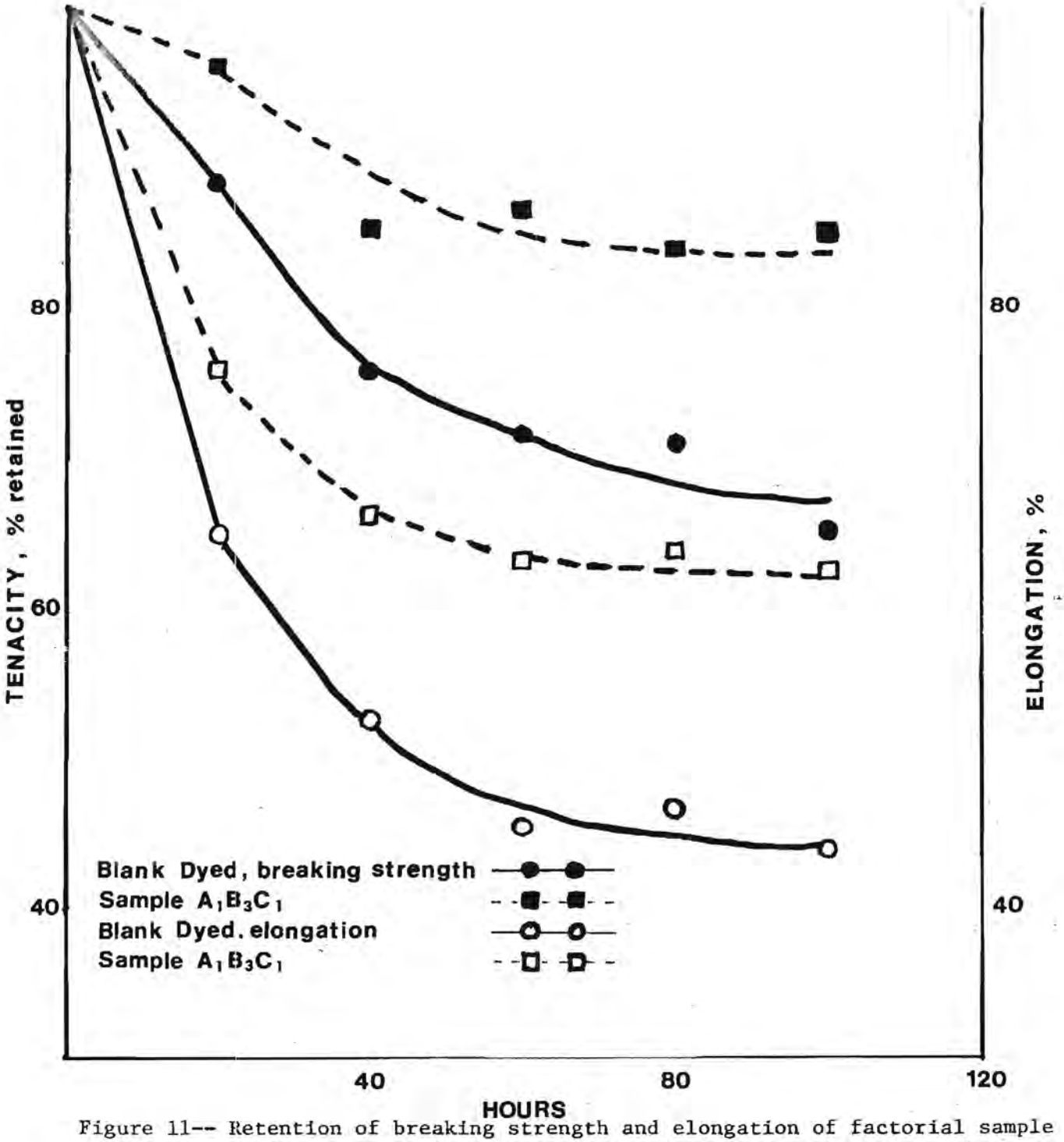


Figure 11-- Retention of breaking strength and elongation of factorial sample $A_1B_3C_1$ compared to control ($A_oB_oC_o$) on exposure to the carbon-arc fadeometer

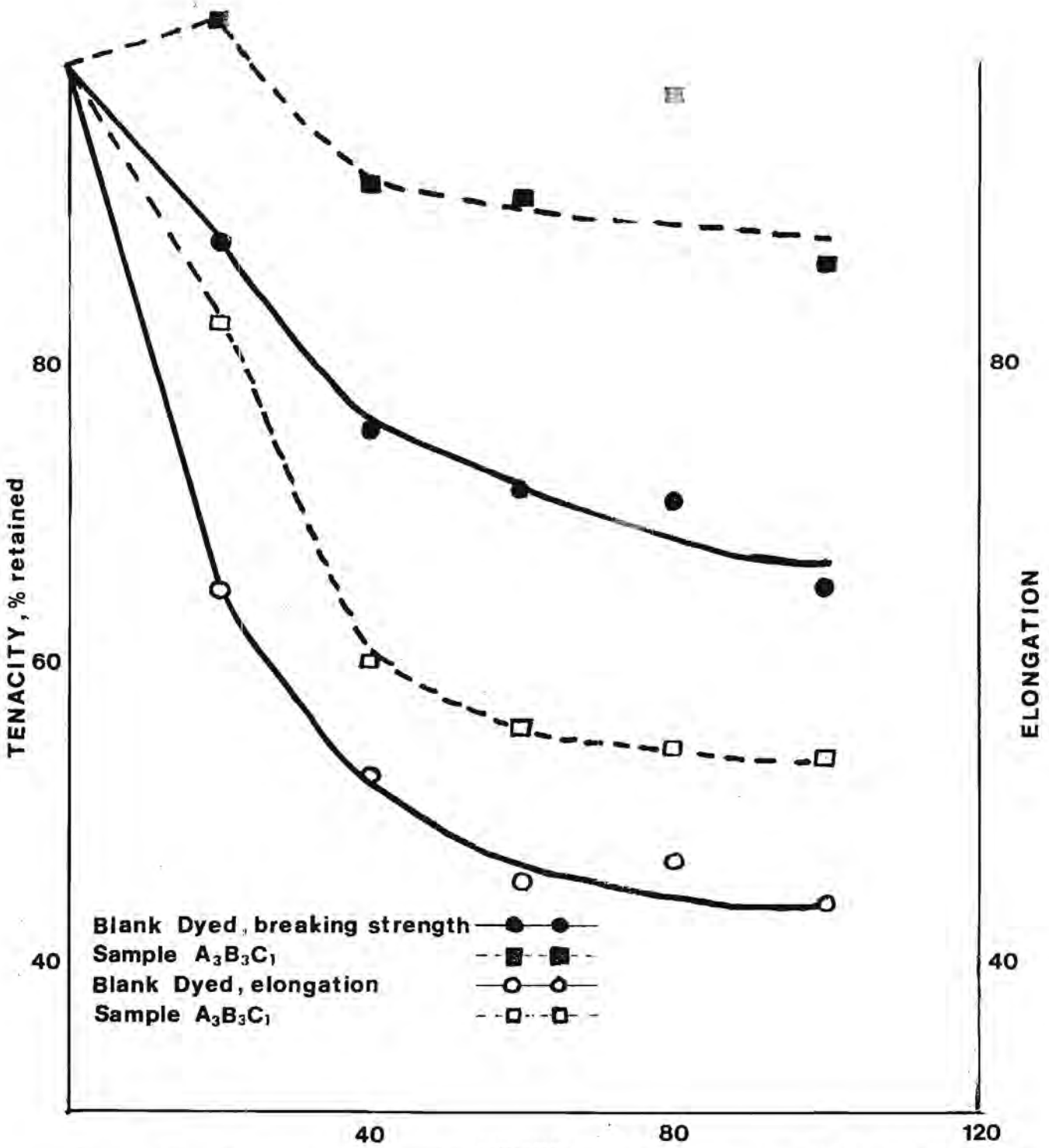


Figure 12-- Retention of breaking strength and elongation of factorial sample $A_3B_3C_1$ compared to control ($A_oB_oC_o$) on exposure to the carbon-arc fadeometer

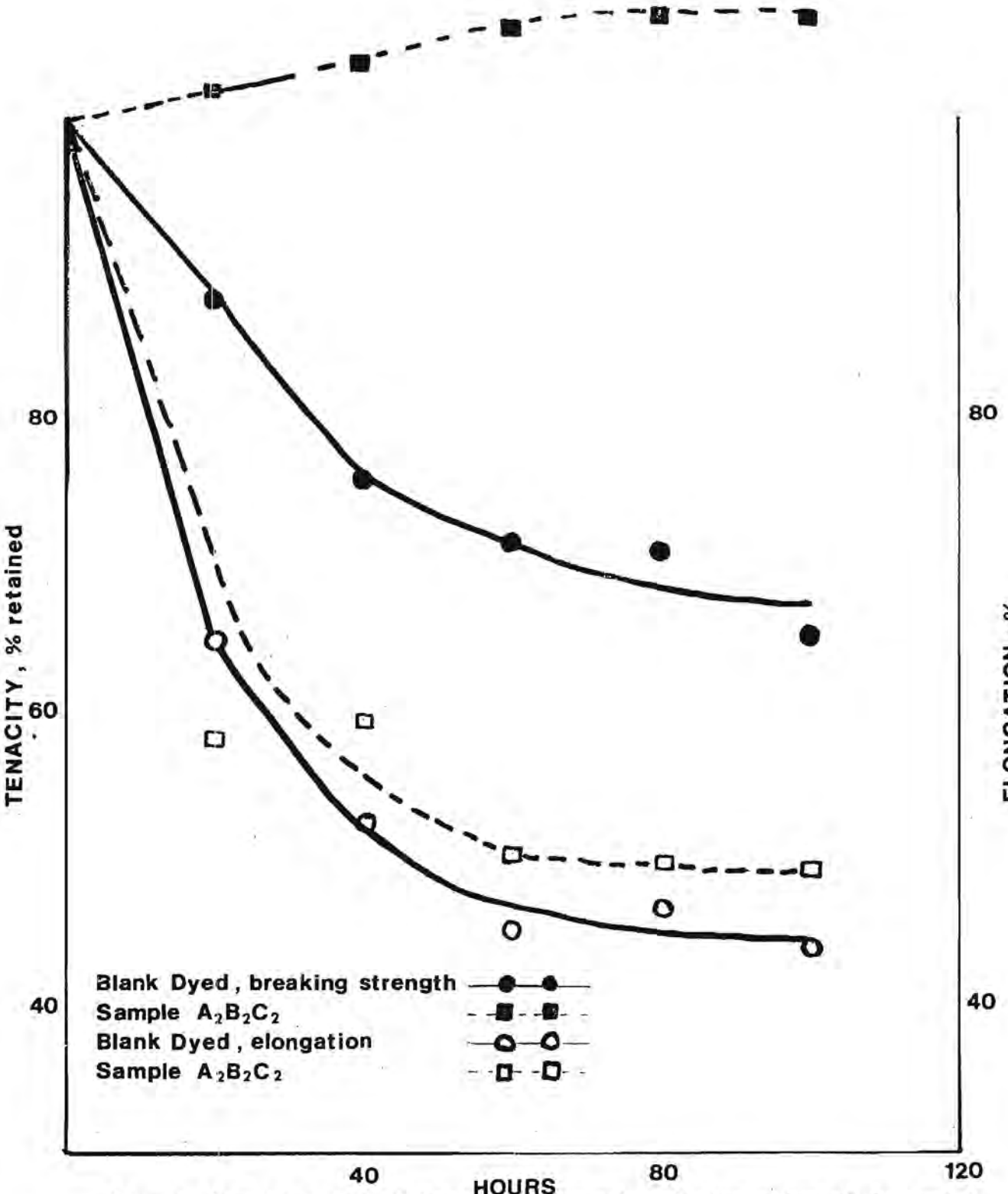


Figure 13-- Retention of breaking strength and elongation of factorial sample $A_2B_2C_2$ compared to control ($A_oB_oC_o$) on exposure to the carbon-arc fadeometer

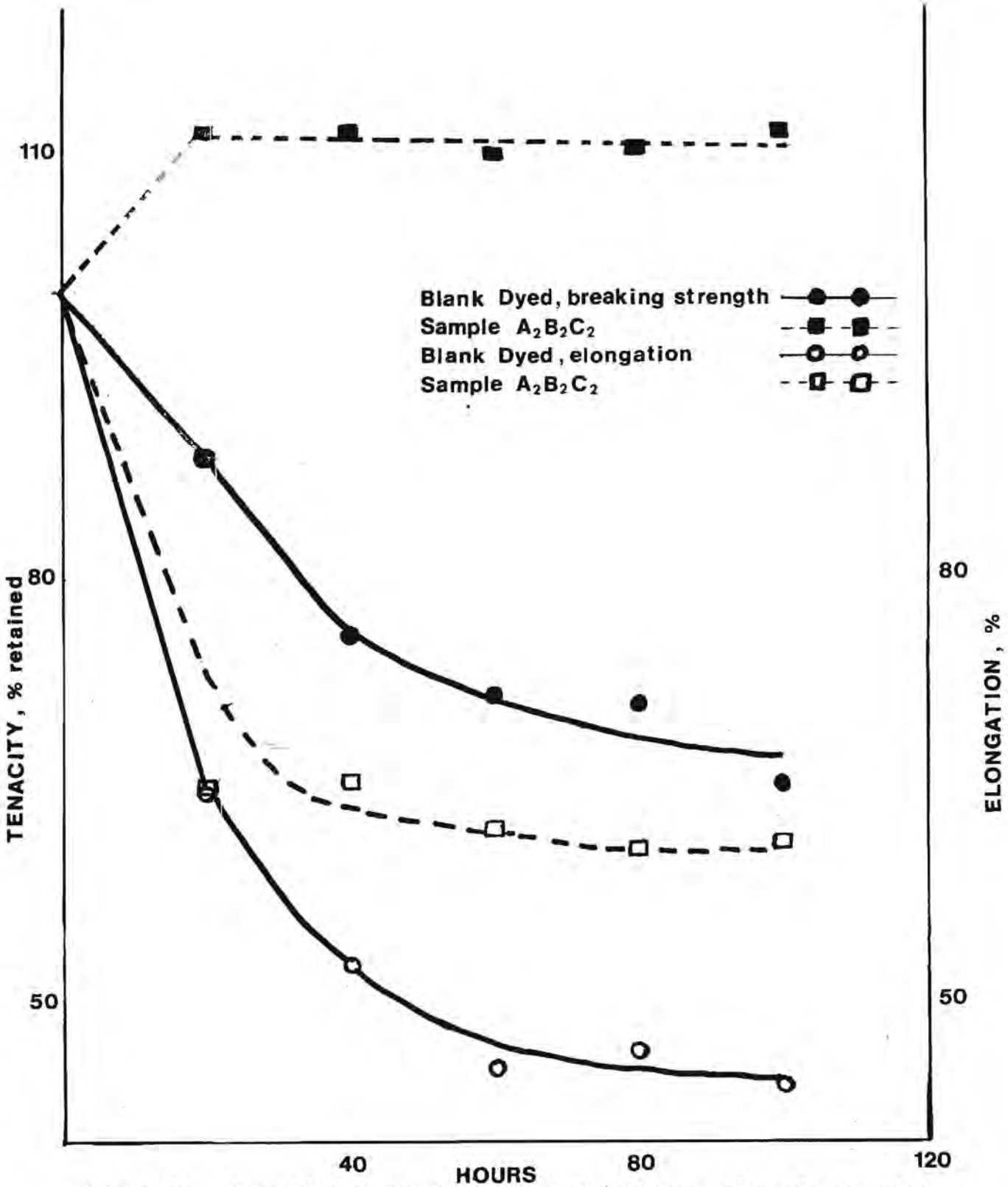
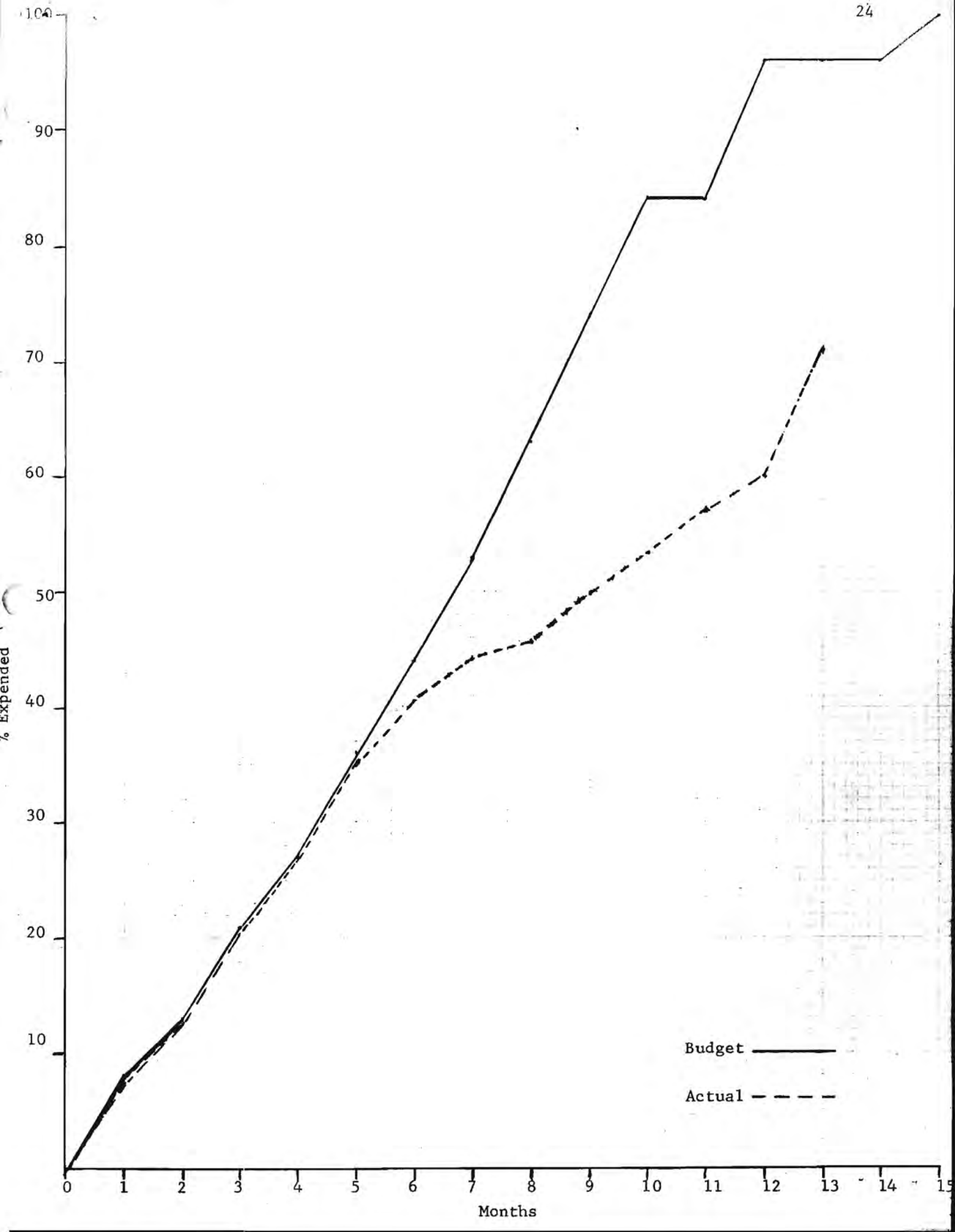


Figure 14-- Retention of breaking strength and elongation of factorial sample $A_2B_2C_2$ compared to control ($A_oB_oC_o$) on exposure to the carbon-arc fadeometer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Actual

E-27-623

Monthly Progress Report Number 14

(July 26, 1975 - August 26, 1975)

Development of Ultraviolet Protection Nomex

Life Support SPO
Air Force Systems Command
Aeronautical Systems Division
Wright-Patterson Air Force Base, Ohio 45433

(Prepared Under Contract No. F33657-74-C-0716
by
Georgia Institute of Technology
Atlanta, Georgia 30332
W. C. Tincher, author)

Summary

Detailed analysis of the factorial experiment for selection of systems for stabilization of Nomex against UV degradation has been completed. The analysis has led to the selection of the following systems for further investigation in Phase II of the project:

1. Blancophor AW 33%, Tinuvin P 33%, Oxanilide 33%
2. Blancophor AW 15%, Tinuvin P 50%, Oxanilide 33%
3. Tinuvin P 50%, Oxanilide 33%
4. Tinuvin P 50%

The selection of these systems completes Phase I of the project. However, as interesting stabilizer candidates become available they will be screened for activity in reducing Nomex UV degradation.

Fabric samples (10 inches by 72 inches, minimum) will be prepared containing the stabilizer systems above for testing by both the Air Force and Georgia Tech laboratories.

A meeting to discuss the results of the factorial experiment and to review plans for Phase II of the project was held at Wright-Patterson Air Force Base on August 28. Samples to be prepared for Phase II and test procedures were discussed.

Table of Contents

I. Introduction

Major effort this month has been directed toward completion of the analysis of the factorial experiment for selection of UV stabilizer systems for Nomex. The purpose of the factorial experiment was to assess the effect of concentration of the stabilizers on light stability and to determine if beneficial interactive effects between stabilizers are observed. Preliminary analysis suggested the need for data on an additional sample containing 10% of each of the 3 selected stabilizers (Blancophor AW, Tinuvin P, and Oxanilide). This sample was prepared and tested and the results included in the final analysis of the factorial experiment. Based on this analysis four stabilizer systems have been selected for further study.

II. Analysis of the Factorial Experiment

Results of the central composite design experiment for testing three stabilizers (Blancophor AW, Tinuvin P, and Oxanilide) at four concentration levels (0%, 33%, 66%, and 100%) are shown in Table I. All data were obtained on samples of Nomex sage green fabric (Mil-C-38351, Type II Class 1). Treated samples were exposed for periods of 0, 20, 40, 60, 80 and 100 hours and tested by the 1" ravel strip method in the warp direction.

Results are reasonably consistent with a few exceptions. Several samples at the 60 hour exposure time ($A_3B_1C_1$, $A_3B_1C_3$) show unusually low strengths. Data at 80 and 100 hours for these samples suggest that some problem of an undetermined origin is responsible for the low values at the 60 hour exposure time. Sample $A_1B_3C_1$ shows extremely high values for the strength both initially and after all exposure times. The reason for these unusually high values is not apparant.

Table I. Average Strength Measured at Various UV Exposure Levels for All Treatment Combinations

Treat. Comb.	Average Strength at Fadeometer Hours					
	0	20	40	60	80	100
$A_oB_oC_o$	224	198	170	160	159	146
$A_1B_1C_1$	244	219	213	199	199	197
$A_1B_1C_3$	234	192	182	186	206	213
$A_1B_3C_3$	221	240	224	212	201	198
$A_3B_1C_1$	212	184	203	127	162	218
$A_3B_1C_3$	215	206	178	117	180	191
$A_3B_3C_3$	229	230	215	183	207	207
$A_1B_3C_1$	270	260	230	233	227	229
$A_3B_3C_1$	222	229	205	202	217	193
$A_2B_2C_2$	203	217	218	219	220	221

95% Confidence Limit = $\pm$ 14 lbs.

$A_oB_oC_o$ - UV inhibitors not present

$A_1B_1C_1$ - UV inhibitors present in lowest concentrations

$A_3B_3C_3$ - UV inhibitors present in highest concentrations

The effects of concentration of the three stabilizers on UV stability of Nomex fabrics are shown in Figures 1 through 3. The strength after both 40 and 100 hours exposure for samples containing Blancophor AW (Figure 1) suggest that little improvement in strength retention occurs above 33%. In fact there is some indication that higher levels may actually give less strength retention than the 33% level. Similiar results were obtained for Oxanilide as shown in Figure 3. The drop in strength at higher concentration was somewhat more pronounced in this case.

Tinuvin P does not reach maximum effectiveness until approximately 50% OWF is present in the dyebath. There is little difference in strength at the 67 and 100% level (see Figure 2).

The lack of data between 0 and 33% for all additives at least suggested the possibility that lower levels may be as effective as 33%. A sample was prepared, therefore, with 10% of each of the additives in the dyebath. The results for this sample is shown as the dotted circle and circled x in Figures 1-3.

Interactive effects between the stabilizer candidates are shown in Figure 4-9. No pronounced effects are observed between the various components. In general, high levels of B in combination with low levels of A and C gave somewhat higher strengths.

One other important observation made during the factorial experiment was that the Blancophor AW reduced the dye lightfastness of the sage green fabric. Therefore, samples selected for further study included a number of combinations excluding Blancophor AW.

The four systems selected for study in Phase II are:

1. Blancophor AW 33%, Tinuvin P 33%, Oxanilide 33%

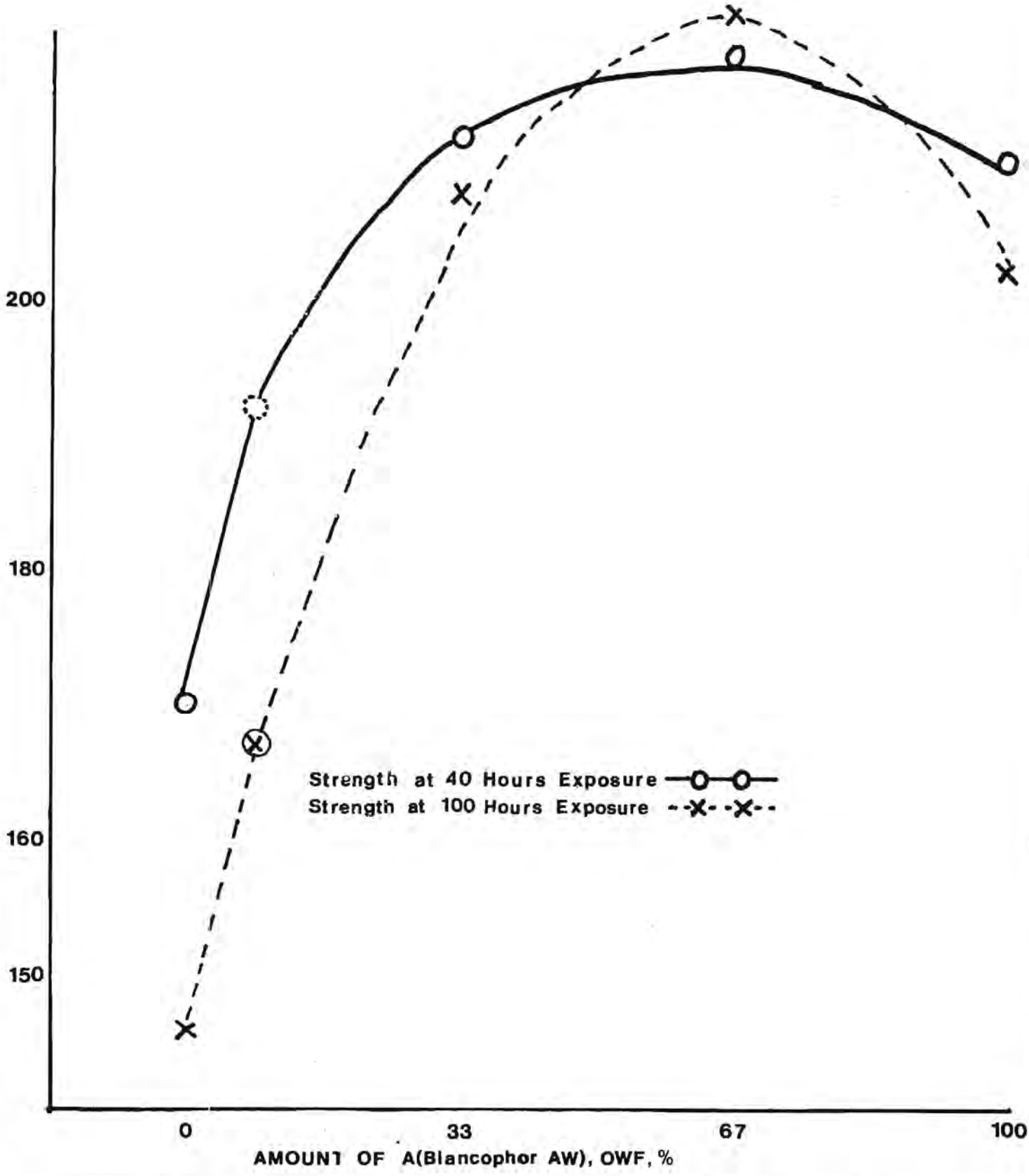


Figure 1 -- The effect of concentration of Blancophor AW on strength of Nomex fabrics after exposure for 40 and 100 hours in the carbon arc fadeometer.

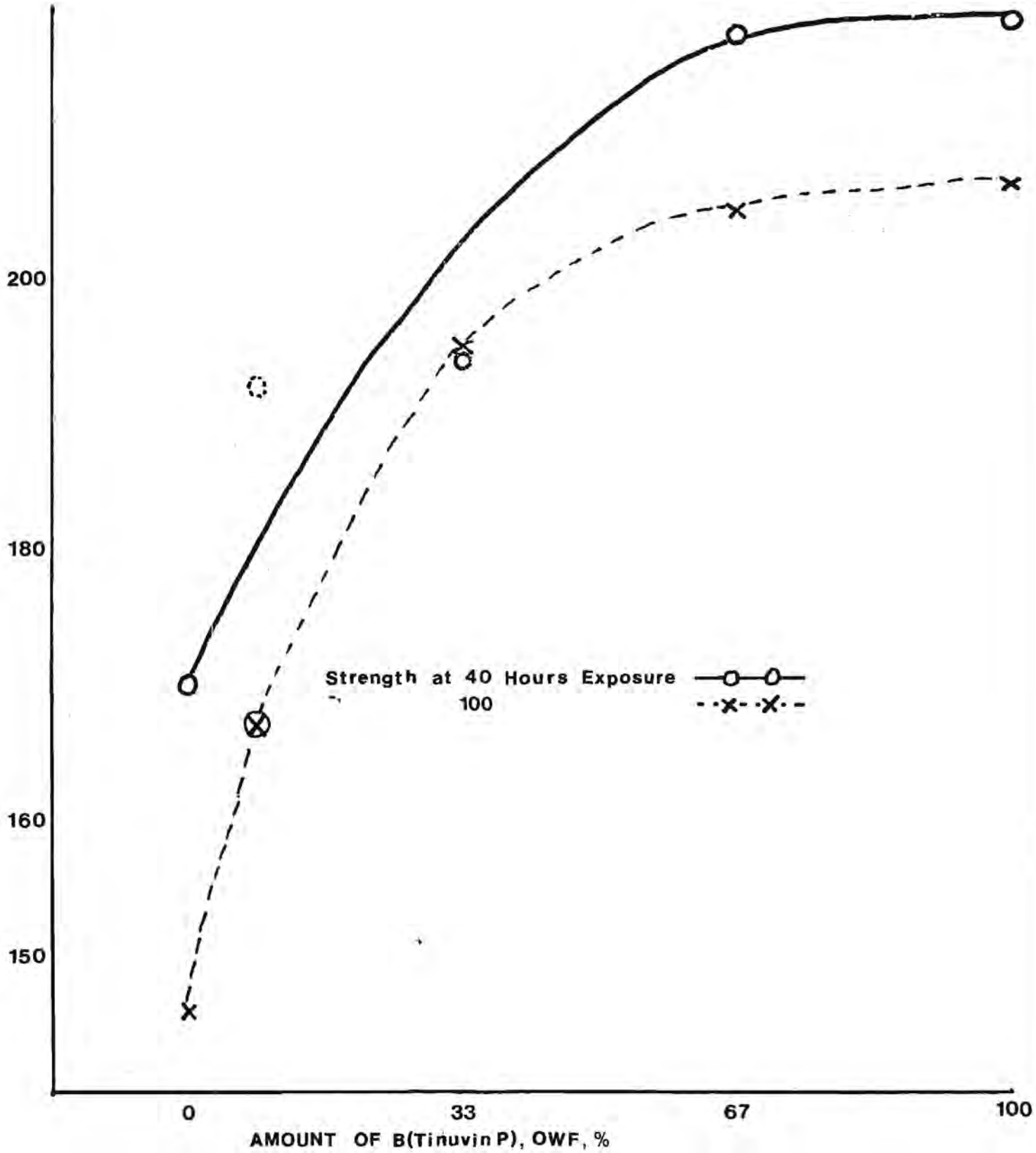


Figure 2 -- The effect of concentration of Tinuvin P on strength of Nomex fabrics after exposure for 40 and 100 hours in the carbon arc fadeometer.

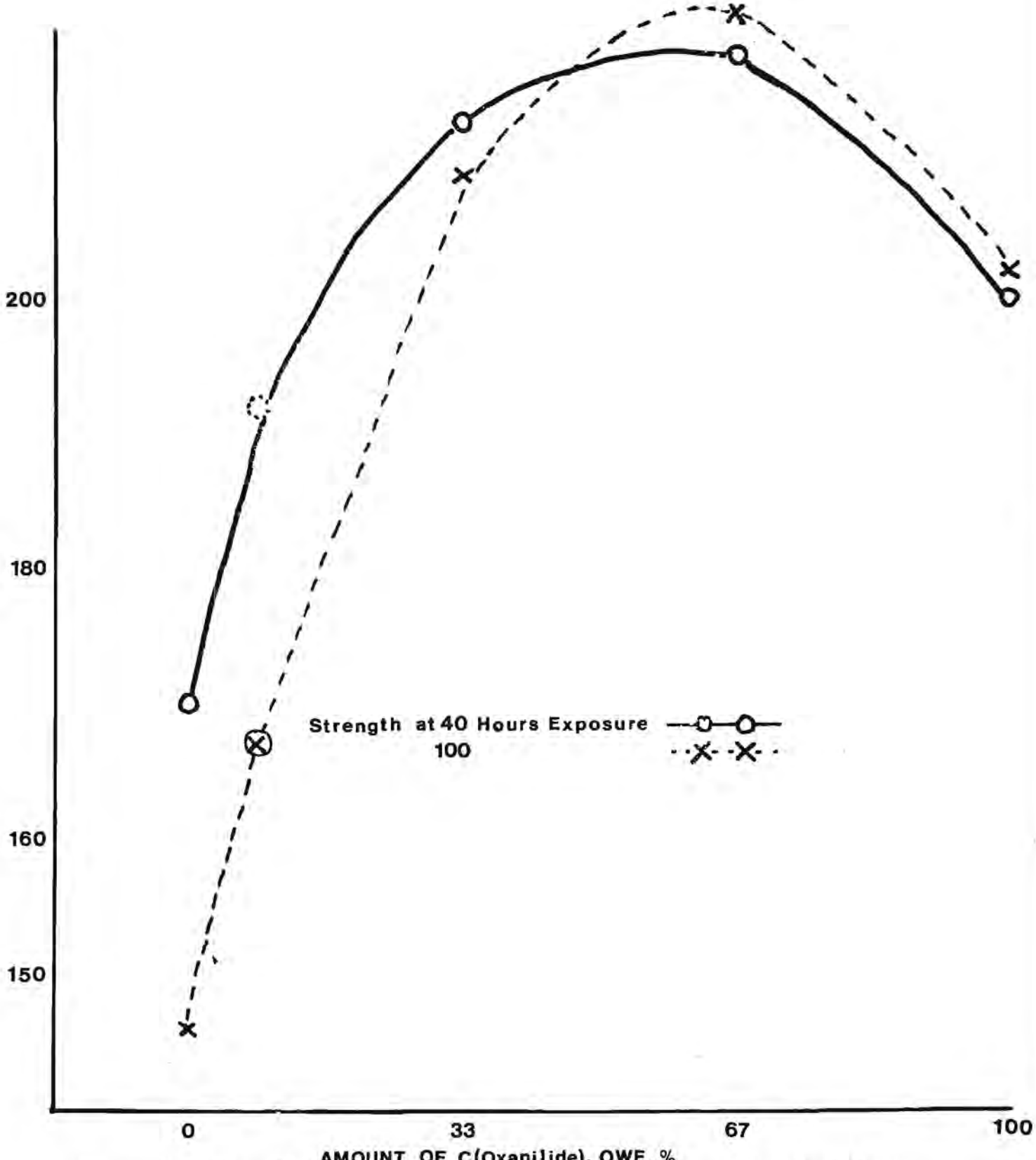


Figure 3 -- The effect of concentration of Oxanilide on strength of Nomex fabrics after exposure for 40 and 100 hours in the carbon arc fadeometer.

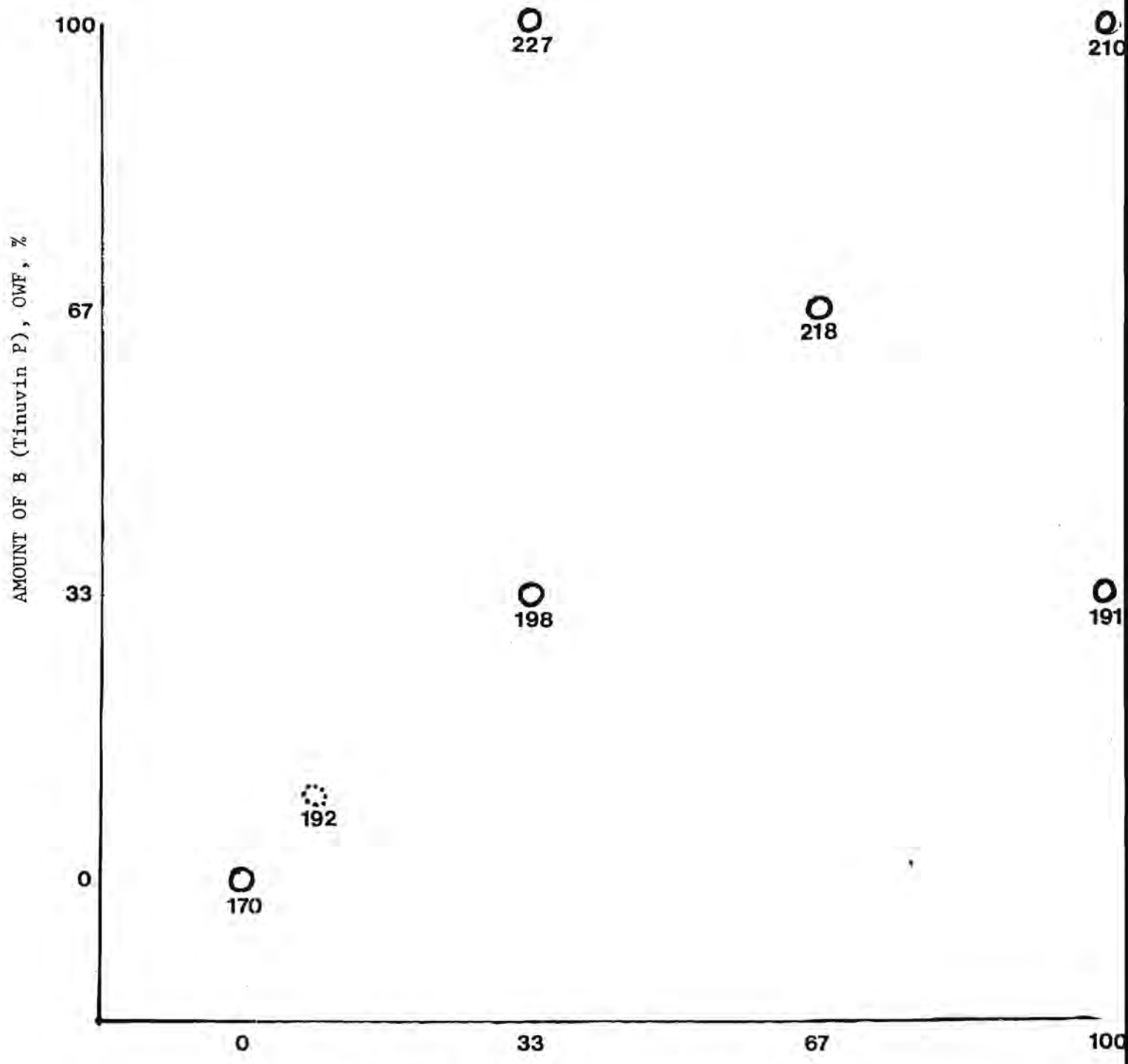


Figure 4 -- Strength after 40 hours exposure of fabric samples containing Blancophor AW and Tinuvin P.

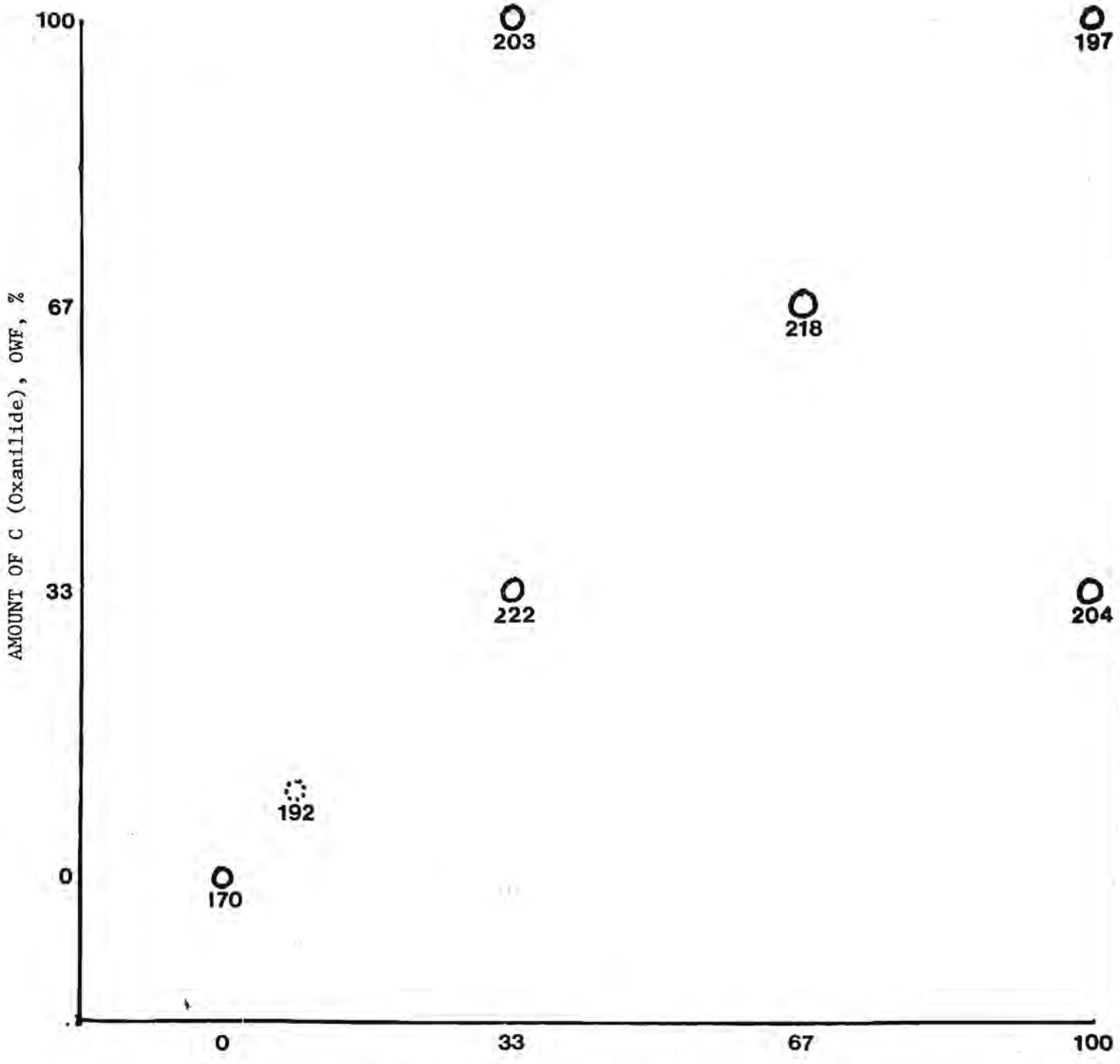


Figure 5 -- Strength after 40 hours exposure of fabric samples containing Oxanilide and Blancophor AW.

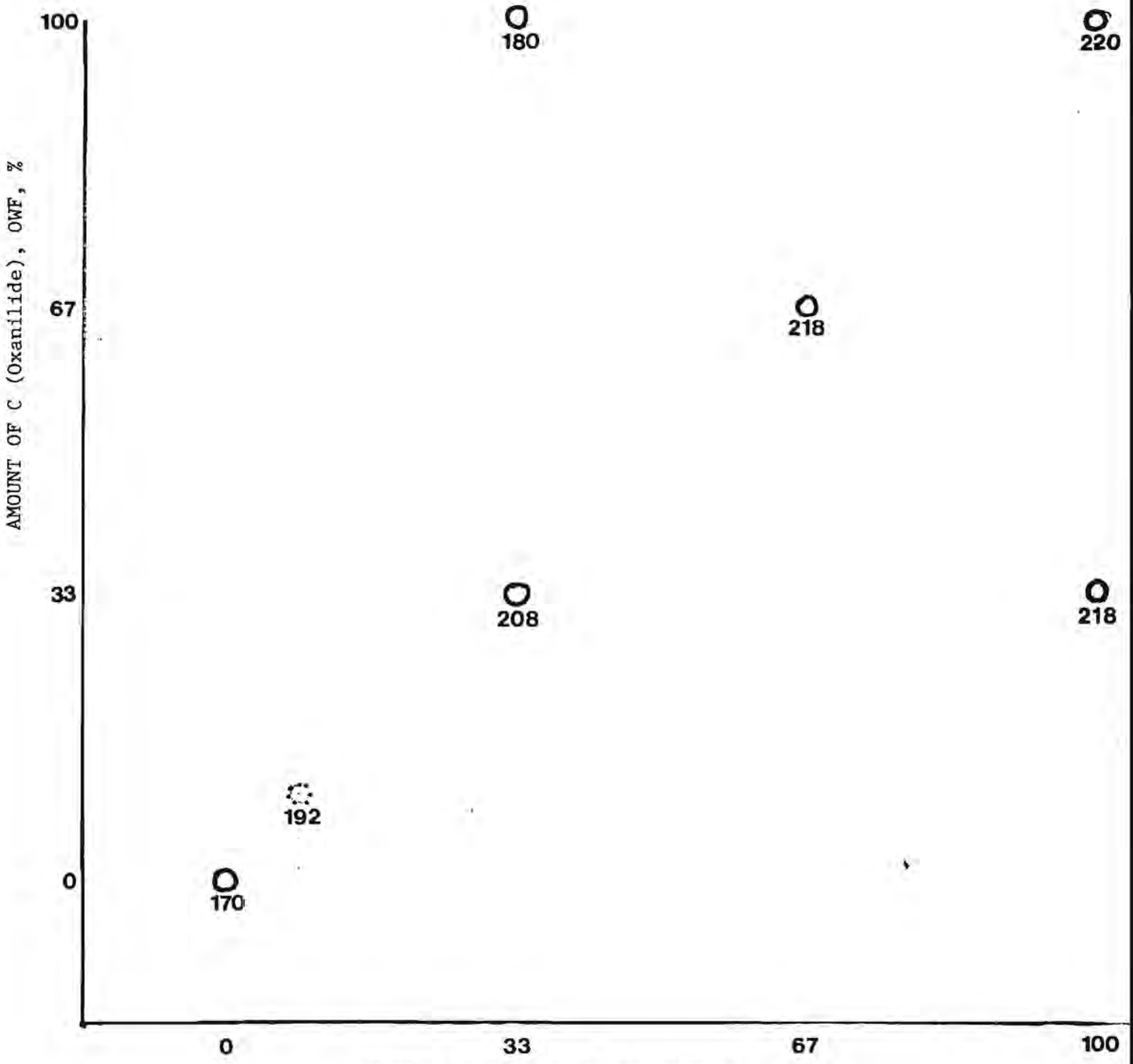


Figure 6 -- Strength after 40 hours exposure of fabrics samples containing Oxanilide and Tinuvin P.

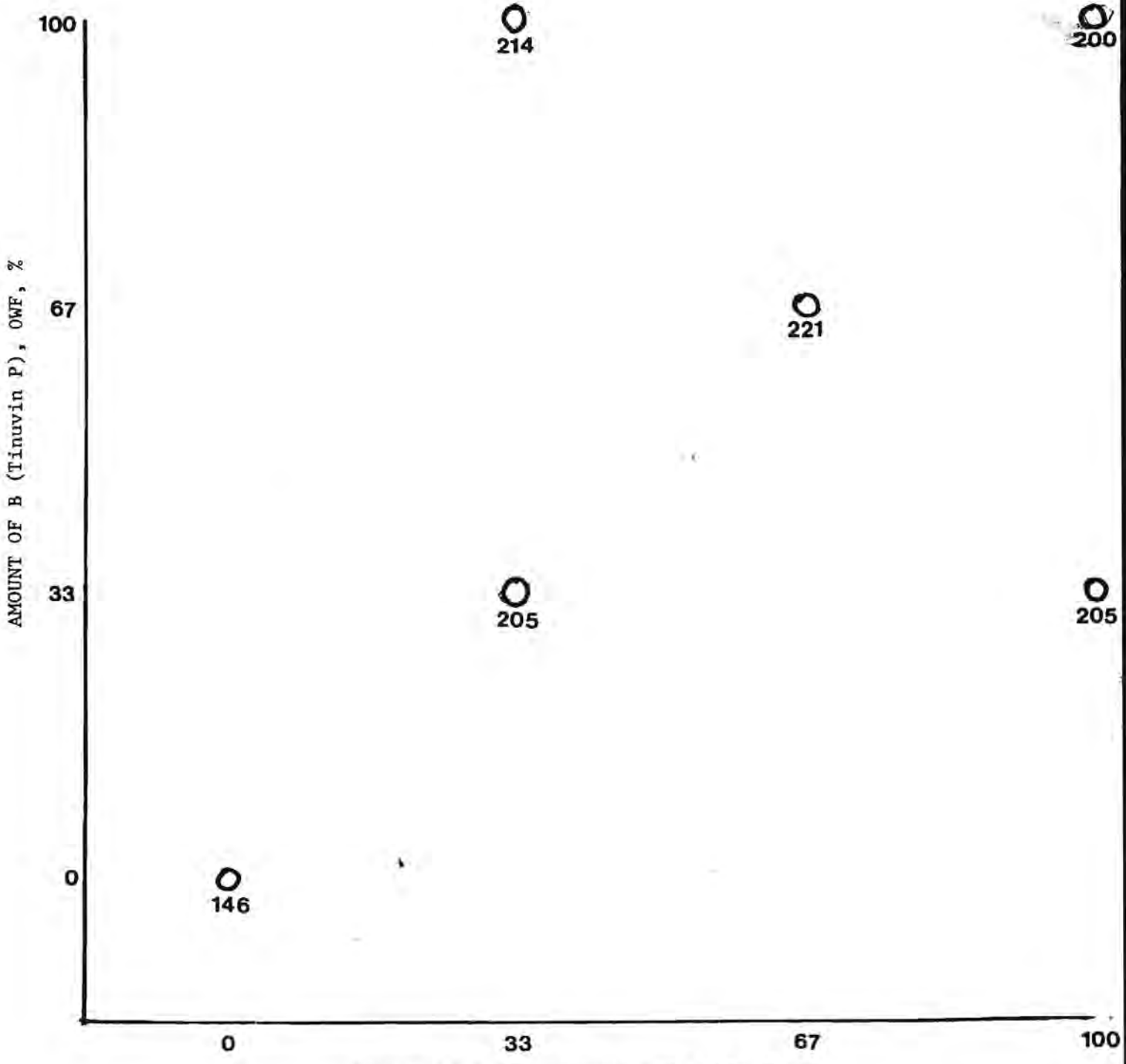


Figure 7 -- Strength after 100 hours exposure of Nomex fabric containing Blancophor AW and Tinuvin P.

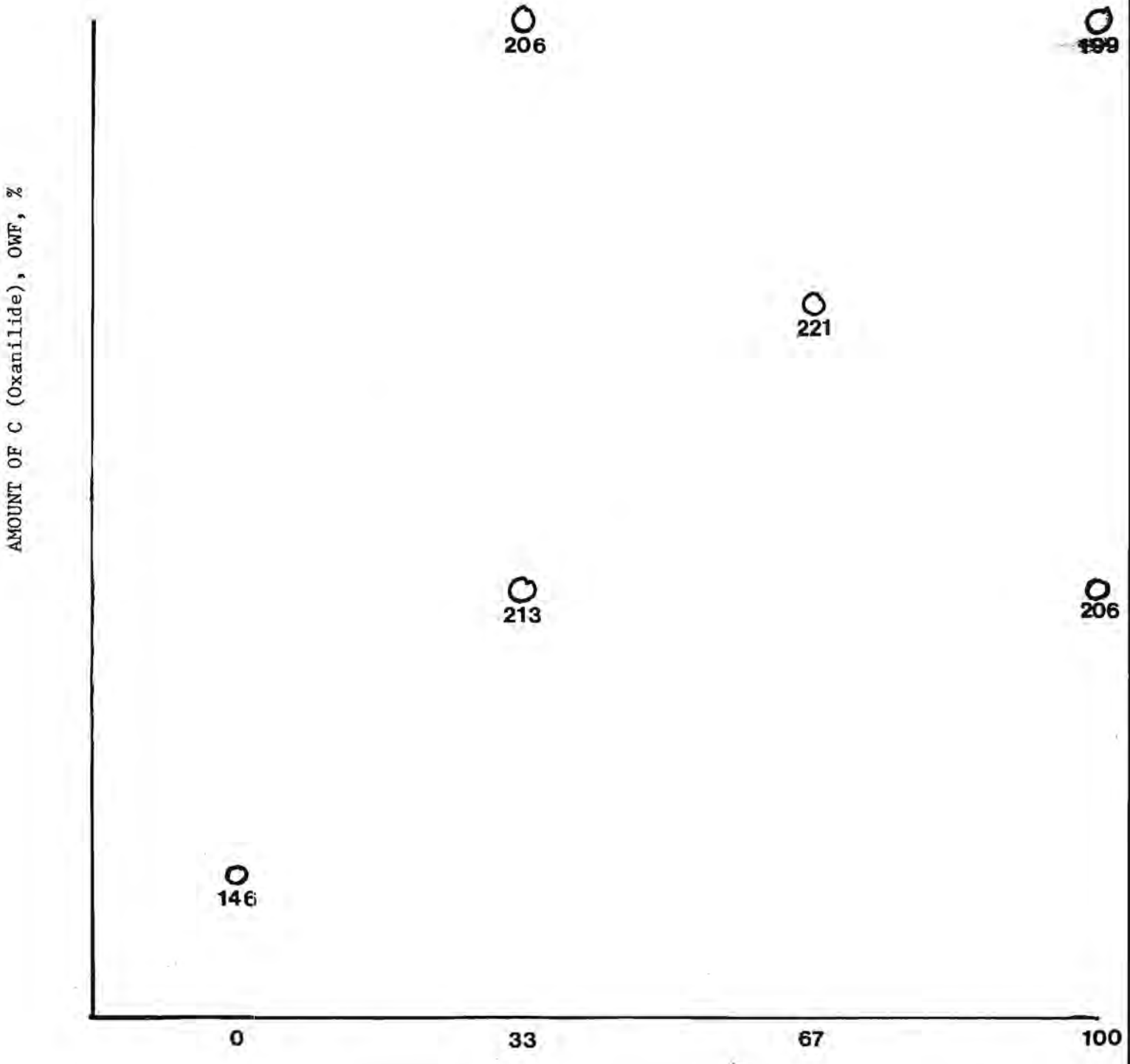


Figure 8 -- Strength after 100 hours exposure of Nomex fabrics containing Oxanilide and Blancophor AW

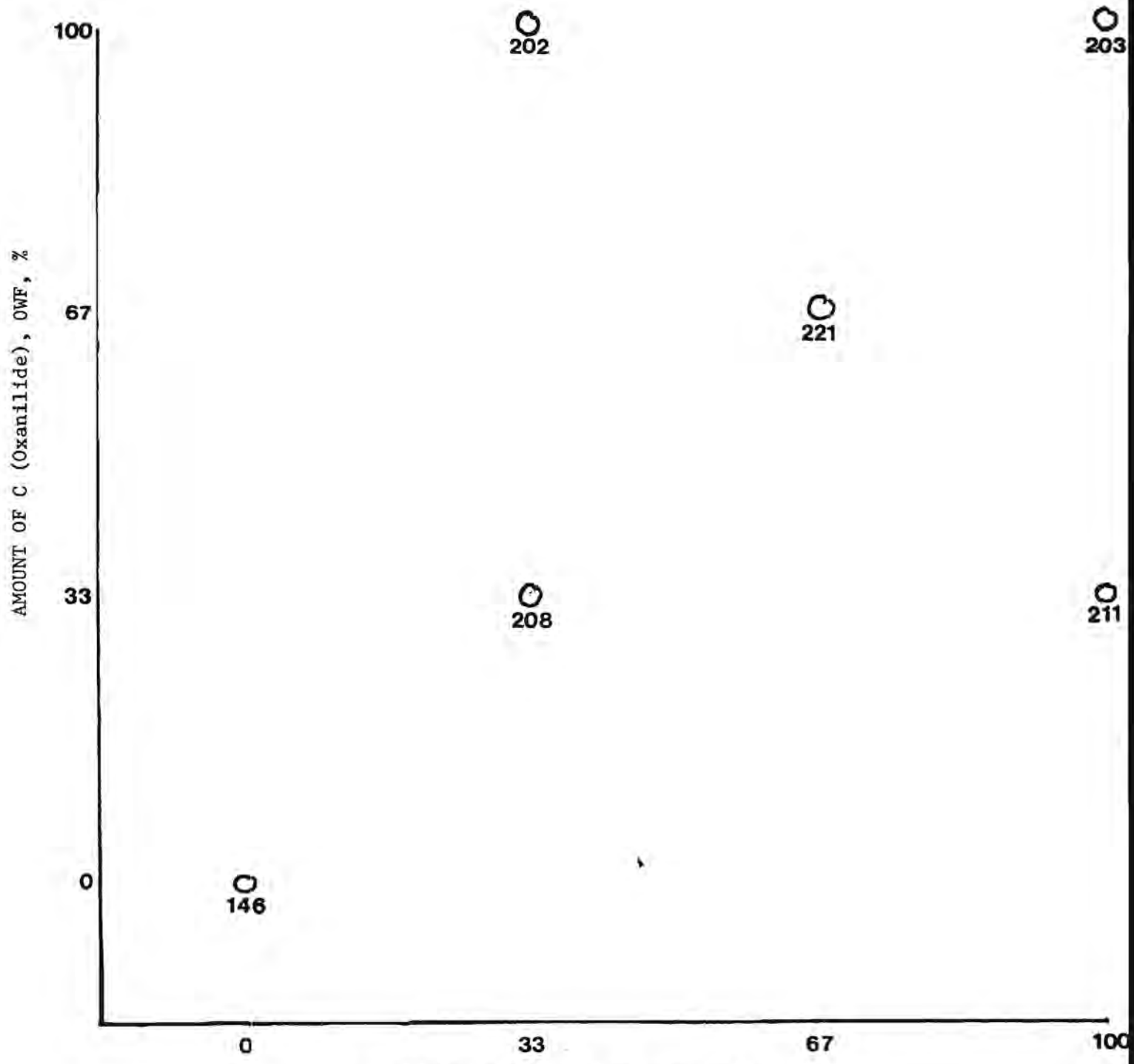


Figure 9 -- Strength after 100 hours exposure of Nomex fabrics containing Oxanilide and Tinuvin P.

2. Blancophor AW 15%, Tinuvin P 50%, Oxanilide 15%

3. Tinuvin P 50%, Oxanilide 33%

4. Tinuvin P 50%

A number of either criteria were used in selection of these combinations. First, the lowest levels expected to be effective were selected to reduce treatment costs and give lower add-on of chemicals which may adversely affect other properties of the fabric. Second, at least two systems were selected which do not contain Blancophor AW to avoid the reduced dye light-fastness previously mentioned. Third, combinations were selected in which the level of Tinuvin P was usually higher than the other stabilizers. One of the selected systems (number 2 above) is similar to the factorial sample which gave exceptionally high strength values both initially and after exposure.

Fabric samples will be prepared incorporating the four selected systems.

III. Technical Review Meeting

A technical meeting to review progress on the project and to confirm plans for Phase II was held at Wright-Patterson Air Force Base on August 28, 1975. Present at the meeting were Walter Gloor, Lee Brock, Preston Opt and Wayne Tincher.

The results of the factorial experiment were presented and a number of prepared stabilizer systems for Phase II were discussed. It was agreed that the four systems previously mentioned (see Section II above) were the best candidates for study in Phase II.

The testing program for Phase II was also discussed. The Air Force Materials Laboratory will require a minimum of 10 inch by 72 inch samples

for testing. If possible samples 10 inches by 108 inches will be supplied. Samples will be identified only by notebook page number so that the particular stabilizer system will not be known at the time of testing. Samples will be tested for periods up to 200 hours in standard fadeometers. Samples are expected to be ready for testing near the end of September.

The test method to be used in assessing changes in flammability which may occur on treating Nomex fabrics was also discussed. The vertical flame test was thought to be adequate and the contract monitor will inform Georgia Tech if this test method is acceptable.

The method to be used in adding light stabilizers to Nomex fabric was discussed. It was agreed that treatment in a high pressure jig would be an acceptable procedure.

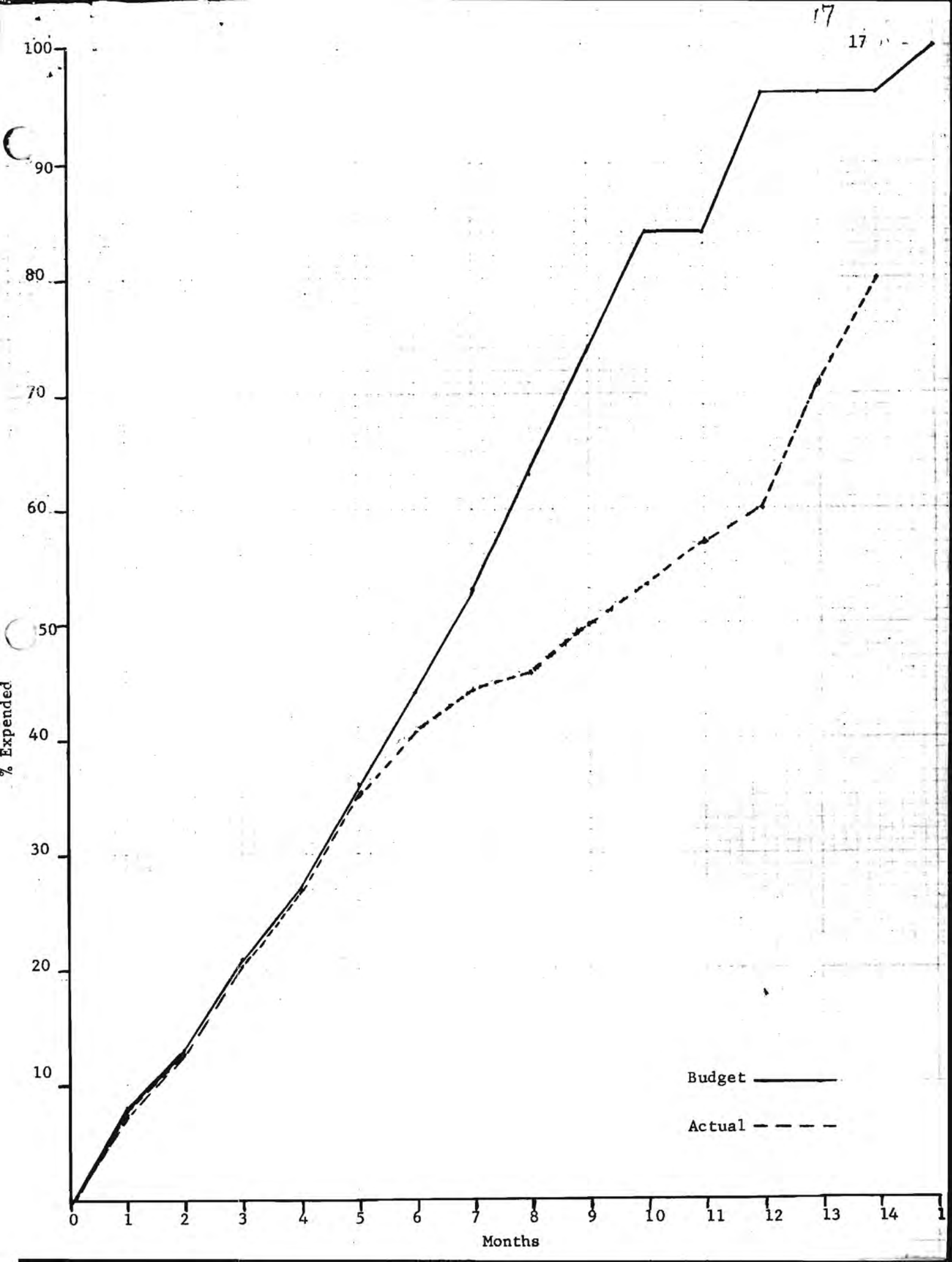
Time of performance on the contract was also discussed. Due to delays in delivering of fiber and fabrics at the beginning of the project and equipment problems (faculty components were supplied by fadeometer manufacturer which caused a significant delay) it will be necessary to request an extension of the time of performance (with no increase in funding). To further expedite completion of the project, it was agreed that the 200 yards of fabric and 100 yards of webbing for Phase III could be ordered immediately.

IV. Future Work

Major effort during the next month will be devoted to preparation of the four test fabrics for Phase II of the project.

V. Budget

The funds budgeted and either expended or allocated for the first fourteen months are shown on the attached graph.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E-27-623

Monthly Progress Report Number 15

(Aug. 26, 1975 - Sept. 26, 1975)

Development of Ultraviolet Protection Nomex

Life Support SPO
Air Force Systems Command
Aeronautical Systems Division
Wright-Patterson Air Force Base, Ohio 45433

(Prepared Under Contract No. F33657-74-C-0716
by
Georgia Institute of Technology
Atlanta, Georgia 30332
W. C. Tincher, author)

Summary

Three yard samples of Nomex sage green fabric (Mil-C-38351, Type II Class 1) have been treated with four systems for improving the UV stability. The four systems are:

1. Blancophor AW 33%, Tinuvin P 33%, Oxanilide 33%
2. Blancophor AW 15%, Tinuvin P 50%, Oxanilide 15%
3. Tinuvin P 50%, Oxanilide 33%
4. Tinuvin P 50%

The treatments were applied in a pressure jig dyeing machine at 260 F. Chemocarrier FPN was used as a dyeing assistant.

Samples of the 4 treated fabrics, a blank-dyed fabric and an untreated fabric have been prepared for shipment to the Air Force for evaluation.

Table of Contents

I. Introduction

Major effort this month has been directed toward preparation of fabrics containing the four stabilizer systems selected for Phase II of the project at the technical review meeting held on August 28. These fabrics are now ready for shipment to the Air Force for evaluation.

II. Preparation of Phase II Fabrics

The four systems selected for study in Phase II of the project are shown below:

	% OWF		
	Blancophor AW	Tinuvin P	Oxanilide
#1	33	33	33
#2	15	50	15
#3	-	50	33
#4	-	50	-

Nomex sage green fabric (Mil-C-38351, Type II Class 1) obtained from Stern and Stern Textiles, Inc. was used in preparation of all samples. Pieces 10 inches by 15 yards (approximately 700 grams) were cut from the fabric and treated in a sample size Smith Engineering pressure jig dyeing machine. The fabric was attached to one of the jig rollers with surgical tape and the controller set to automatically cycle the fabric back and forth through the bath. The bath is filled with 29 liters of water and heated to the boil by means of an enclosed steana coil. Additives for a given run were weighed into a large beaker and mixed with 500 ml of the dyeing assistant, Chemocarrier FPN. The well dispersed additives were then

added to the hot dyebath by pouring 1/4 of the mixture alternately in the two sides of the bath during one complete cycle of the jig. The jig was then closed and the pressure raised to 21-23 pounds per square inch (260 F) by injecting live steam into the bath. The fabric was cycled through the bath for 2 hours.

At the conclusion of the treatment cycle the fabric was washed at least 3 times in a standard washer and tumble dried to remove excess dyeing assistant and treatment chemicals.

Some disadvantages of the treatment system were noted during preparation of these samples. The dyeing assistant used was not properly emulsified for use in a low agitation system such as the pressure jig. Accumulation of solids during the treatment cycle made cleanup of the jig and the fabric at the end of the treatment a major problem. A new experimental dyeing assistant formulation has been obtained from Tanatex Chemical Company and will be evaluated as a solution to this problem.

A survey of dyeing systems that would be useful for Nomex treatment has been conducted and a jet dyeing machine will be evaluated for this purpose. A jet machine with the high agitation of the dye liquor may offer some advantages over the pressure jig.

A sample of the fabric as received, a sample of the fabric blank-dyed, and the four treated fabric samples have been prepared and will be delivered to Air Force Materials Laboratory in the near future.

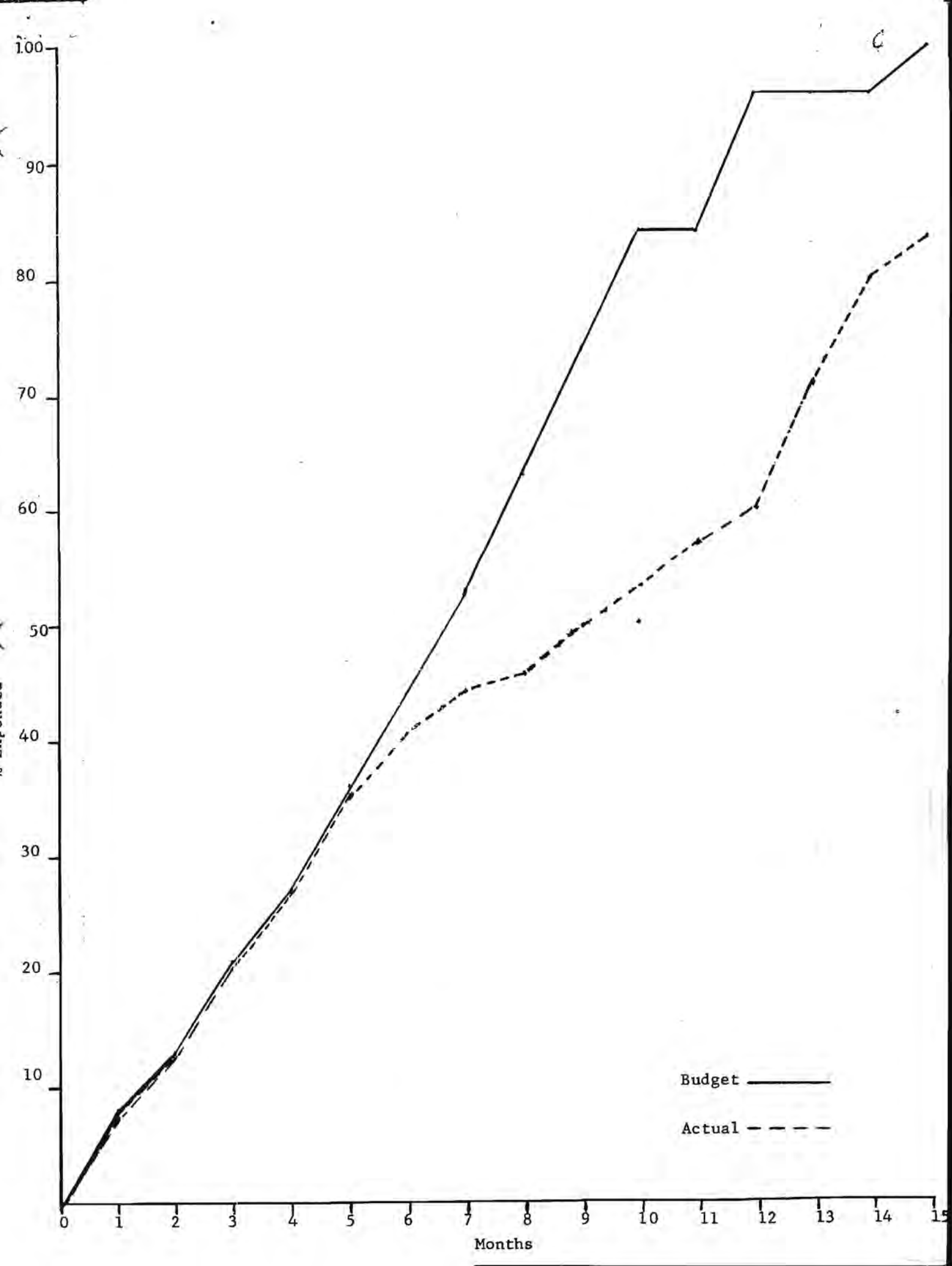
III. Future Work

An evaluation of a new dyeing assistant for the pressure jig and evaluation of the UV stability and properties of treated fabrics are

planned for the next month. Orders for fabric and webbing for Phase III of the project will be placed.

IV. Budget

The funds budgeted and either expended or allocated for the first fifteen months are shown on the attached graph.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E-27-623

Monthly Progress Report Number 16

(Sept. 26, 1975 - Oct. 26, 1975)

Development of Ultraviolet Protection Nomex

Life Support SPO
Air Force Systems Command
Aeronautical Systems Division
Wright-Patterson Air Force Base, Ohio 45433

(Prepared Under Contract No. F33657-74-C-0716
by
Georgia Institute of Technology
Atlanta, Georgia 30332
W. C. Tincher, author)

Summary

Initial testing of the Nomex sage green fabrics (Mil-C-3835, Type II Class 1) treated with four systems for improving the UV stability showed significant improvement in resistance to UV degradation. One of these retained 75% breaking strength after 150 hours exposure in the carbon-arc fadeometer which was the target objective of the project.

Samples of the four treated fabrics, a control, and a "blank-dyed" sample were delivered to the Air Force Materials Laboratory on October 10, 1975.

Table of Contents

I. Introduction

Major effort this month has been directed toward testing of fabrics treated with the four stabilizer systems selected for study in Phase II of the project. Samples of each of these treated fabrics, a control sample and a blank-dyed sample were delivered to the Air Force on October 10, 1975.

II. Sample Identification

The sample identification numbers for the treated and control samples are listed below.

Sample Number	Treatment
109-68-D	Control
109-68-A	Blank-dyed
109-68-E	33% Blancophor AW, 33% Tinuvin P, 33% Oxanilide
109-68-F	15% Blancophor AW, 50% Tinuvin P, Oxanilide
109-68-C	50% Tinuvin P, 33% Oxanilide
109-68-B	50% Tinuvin P, 15% Oxanilide

Nomex sage green fabric (Mil-C-38351, Type II Class 1) obtained from Stern and Stern Textiles, Inc. was used in preparation of all samples. Pieces 10 inches by 15 yards (approximately 700 grams) were cut from the fabric and treated in a sample size Smith Engineering pressure jig dyeing machine. The control sample received no treatment. The "blank-dyed" sample was subjected to the same dyeing procedure as the treated samples except that no stabilizers were added to the dye bath.

III. Results of Test for Resistance to UV Degradation

All samples were exposed to the carbon-arc fadeometer for periods of 50,

100, 150, and 200 hours. Before and after exposure the breaking load and elongation were determined by the 1" ravel strip method with the Instron tensile tester. Results are shown in Tables 1, 2 and 3. The results are plotted in Figures 1 through 5 where the per cent retention of breaking strength and elongation is plotted for each sample compared to the blank-dyed sample (109-68-A).

These data suggest that samples 109-68-E and 109-68-F showed greater resistance to UV degradation than the control or blank-dyed samples. Sample 109-68-E had 75% retention of breaking strength after 150 hours exposure which was the target objective for this project. Samples 109-68-B and 109-68-C showed less improvement than 109-68-E and 109-68-F. This was undoubtedly due to the presence of Blancophor AW in both samples E and F.

A more detailed analysis of the data will be possible when the results of Air Force testing are available.

IV. Future Work

Other properties of the control and treated samples will be determined next month and a new carrier for Nomex dyeing and a new dyeing procedure (jet-dyeing) will be evaluated in preparation for Phase III of the project.

V. Budget

The funds budgeted and either expended or allocated for the first sixteen months are shown on the attached graph.

Table 1

Breaking Strength and Elongation Before and After UV Exposure

		Hours Exposed				
		0	50	100	150	200
109-68-D	Breaking Load	241.6	161.2	126.2	158.4	132.8
	Elongation	54.0	23.1	16.7	21.5	18.9
109-68-A	Breaking Load	241.3	182.0	131.4	125.2	122.4
	Elongation	54.2	26.2	19.2	23.0	21.8
109-68-E	Breaking Load	247.4	193.0	180.2	186.0	199.0
	Elongation	57.0	29.8	27.3	27.6	28.9
109-68-F	Breaking Load	253.6	196.6	146.0	132.8	149.0
	Elongation	63.2	28.4	27.5	27.2	32.6
109-68-C	Breaking Load	241.4	184.8	120.0	106.6	118.0
	Elongation	54.0	26.1	22.2	23.0	23.0
109-68-B	Breaking Load	218.8	145.2	125.4	130.2	126.6
	Elongation	49.9	25.2	27.2	25.7	25.6

Table 2

TENSILE STRENGTH RETENTION (%)

	Hrs. Exposed			
	50	100	150	200
109-68-D	66.7	52.2	65.6	55.0
109-68-A	75.4	54.5	51.9	50.7
109-68-E	78.0	72.8	75.2	80.4
109-68-F	77.5	57.6	52.4	58.8
109-68-C	76.5	49.7	44.2	48.9
109-68-B	66.4	57.3	59.5	57.9

Table 3

ELONGATION RETENTION (%)

	Hours Exposure			
Sample	50	100	150	200
109-68-D	43	31	40	35
109-68-A	48	35	43	40
109-68-E	52	48	48	51
109-68-F	45	44	43	52
109-68-C	48	41	43	43
109-68-B	51	55	51	58

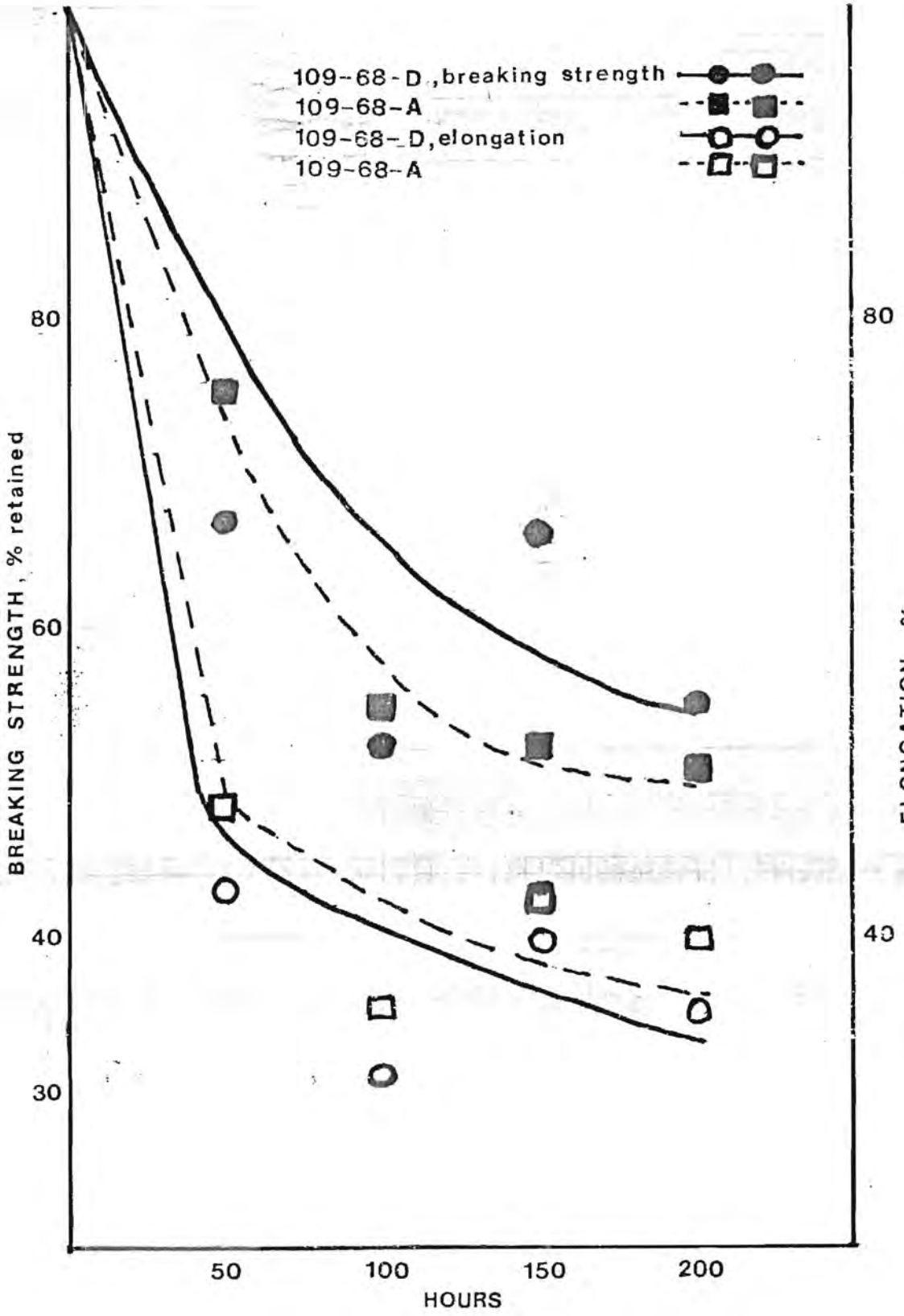


Figure 1--Retention of breaking strength and elongation of blank-dyed (A) and control (D) Nomex fabric after exposure in the carbon-arc fadeometer.

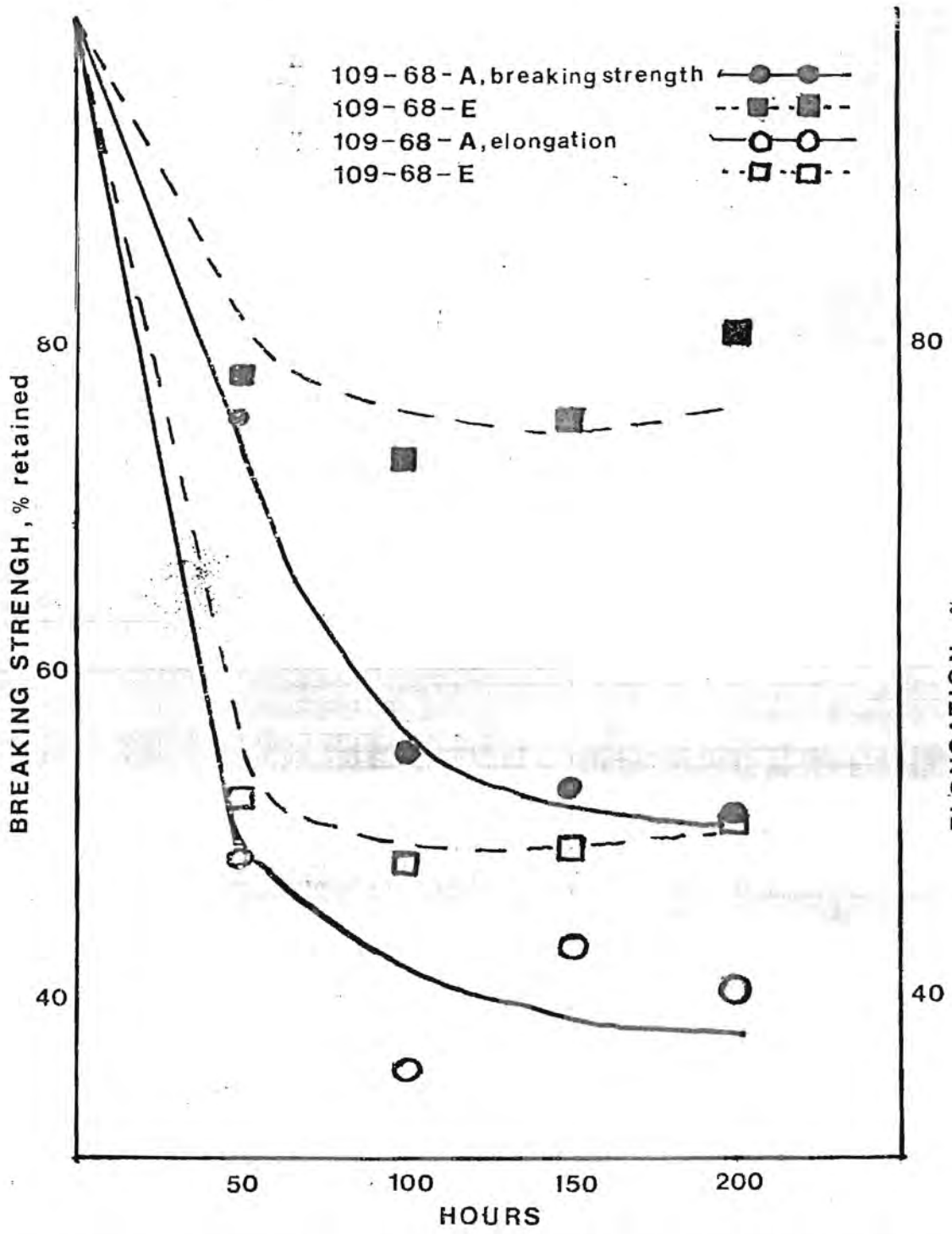


Figure 2--Retention of breaking strength and elongation of treated (E) and blank-dyed (A) Nomex fabric after exposure in the carbon-arc fademeter.

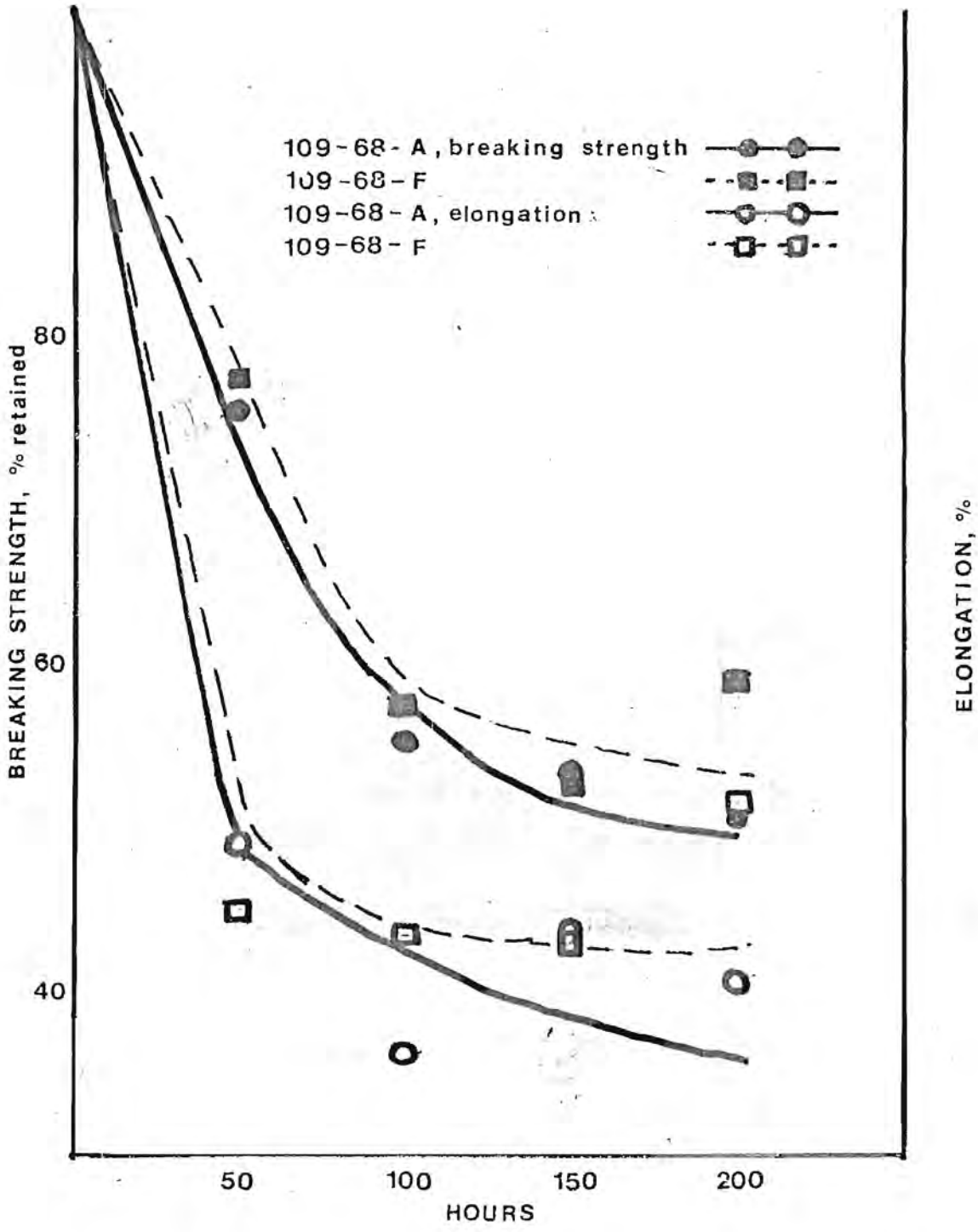


Figure 3--Retention of breaking strength and elongation of treated (F) and blank-dyed (A) Nomex fabric after exposure in the carbon-arc fadeometer.

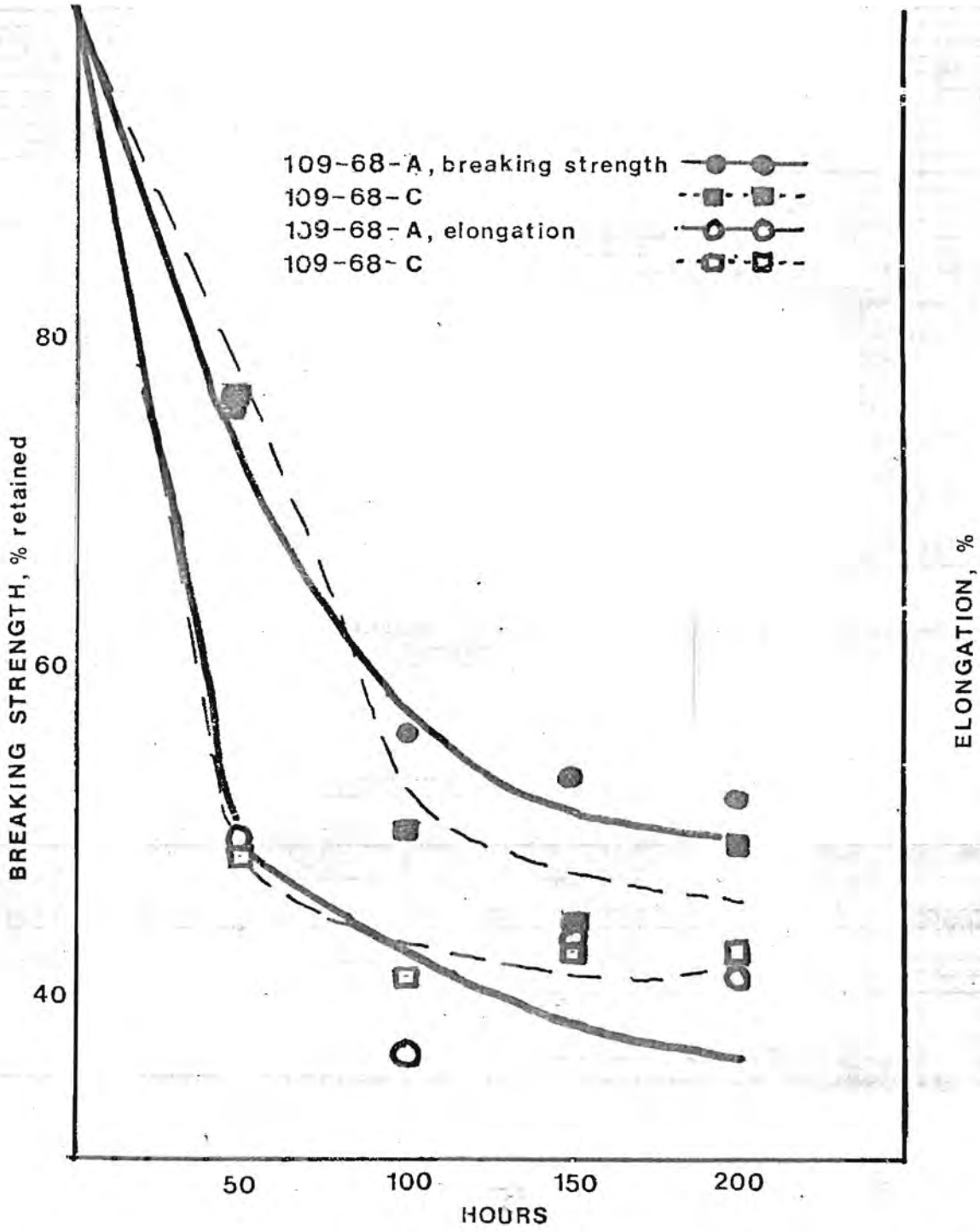


Figure 4--Retention of breaking strength and elongation of treated (C) and blank-dyed (A) Nomex fabric after exposure in the carbon-arc fadeometer.

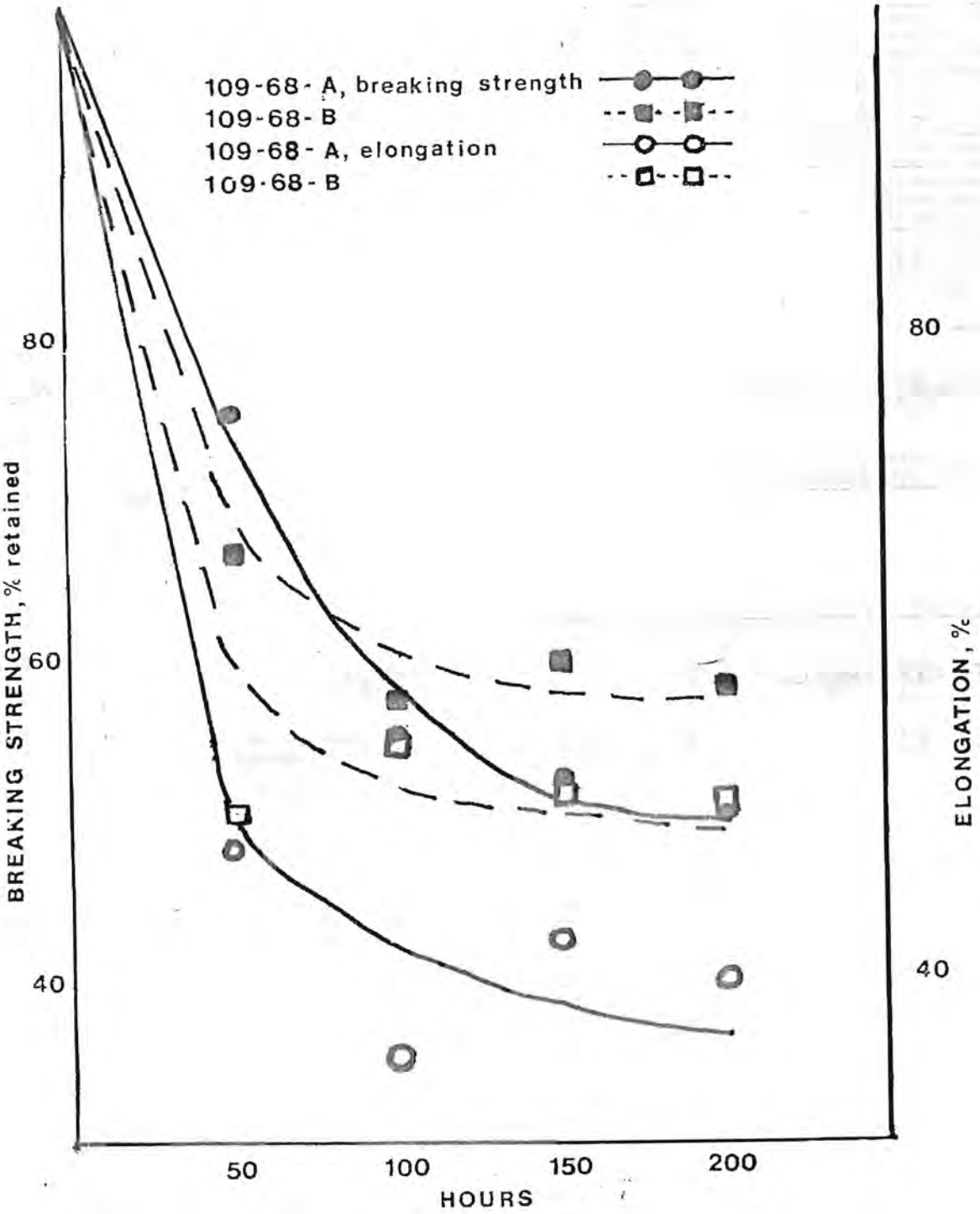
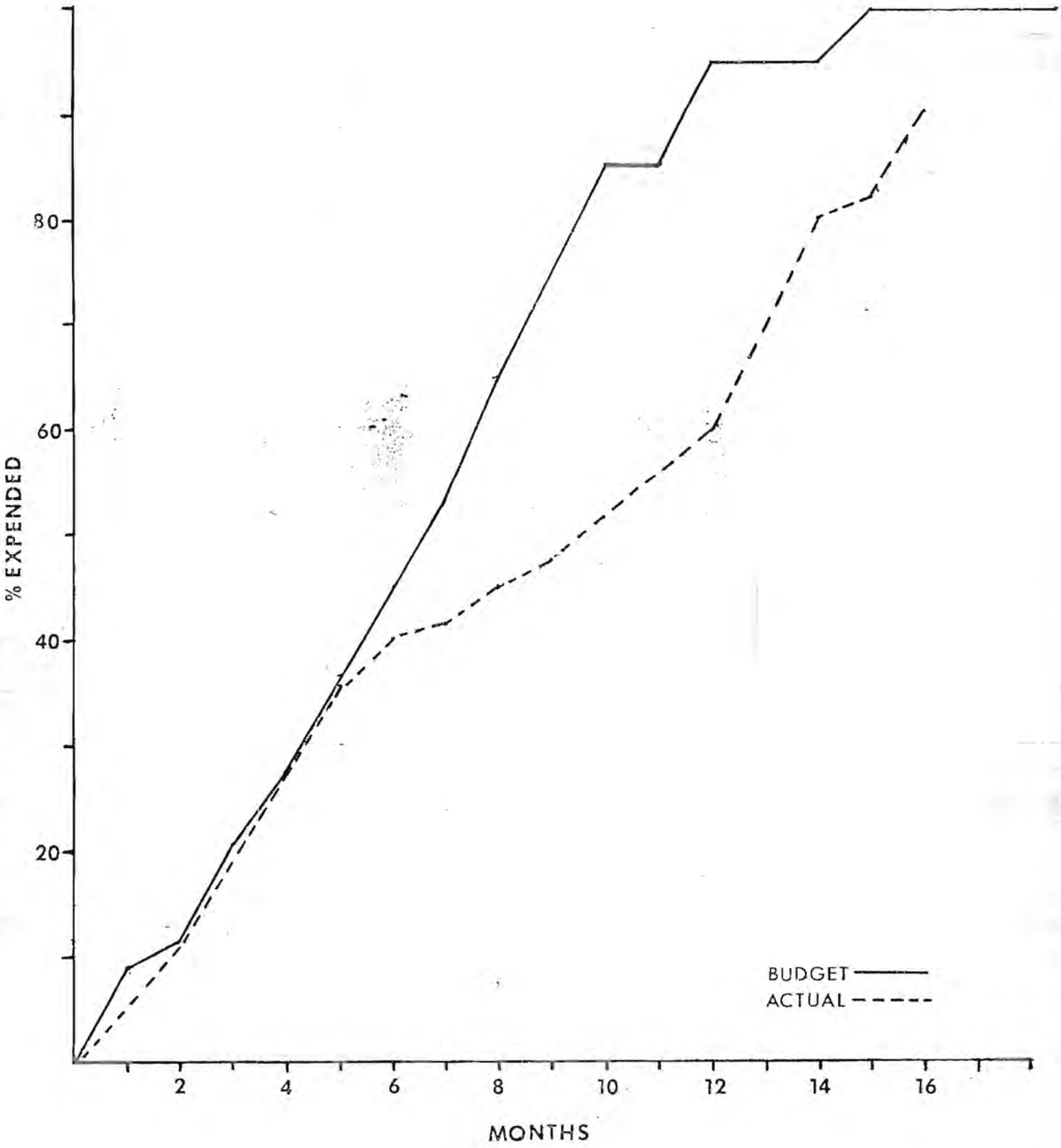


Figure 5--Retention of breaking strength and elongation of treated (B) and blank-dyed (A) Nomex fabric after exposure in the carbon-arc fadeometer.


80
60
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% EXPENDED
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12
14
16
MONTHS

E-27-623

Monthly Progress Report Number 17

(Oct. 26, 1975 - Nov. 26, 1975)

Development of Ultraviolet Protection Nomex

Life Support SPO
Air Force Systems Command
Aeronautical Systems Division
Wright-Patterson Air Force Base, Ohio 45433

(Prepared Under Contract No. F33657-74-C-0716
by
Georgia Institute of Technology
Atlanta, Georgia 30332
W. C. Tincher, author)

Summary

The four treated fabrics, a control, and a "blank-dyed" sample prepared as a part of Phase II have been characterized by a number of procedures to determine the effect on properties of treatments to improve resistance to UV degradation. One unexpected result was that all treated samples showed improved abrasion resistance. One treated sample did have increased char length in the vertical flame test.

In preparation for Phase III of the project a new carrier and a new dyeing procedure (jet-dyeing) were evaluated this month.

A technical review meeting is planned for December 8.

Table of Contents

I. Introduction

An evaluation of the effects of treatment to increase UV stability on other fabric properties has been carried out for the six fabrics prepared as a part of Phase II of the project. The samples evaluated were cut from the 6 fabrics delivered to the Air Force on October 10, 1975. A new dyeing technique (jet dyeing) has also been investigated to determine its effectiveness for incorporation of UV stabilizers in Nomex.

II. Results of Fabric Evaluation

The four treated fabrics, the control, and the blank dyed fabric are identified in Table I. All samples were Nomex sage green fabric (Mil-C-38351, Type II, Class 1). The properties measured and the methods employed are given below.

Yarns per Inch

Warp ends per inch and filling picks per inch were measured as directed in Method 5050, Federal Test Method Standard 191. Results are shown in Table 2 and indicate that fabric construction was identical for all of the experimental fabrics.

Fabric Weight

Weight of the experimentally-treated fabrics was measured according to Method 5041 of Federal Test Method Standard 191. Results are also shown in Table 2 and indicate a large difference in the measured weights among the samples, with the differences being related to the take-up of the UV resistant compound by the fabric.

Thickness

Fabric thickness was measured according to Method 5030. Thickness varied among the several samples approximately the same as fabric weight and again is related to the take-up by the fabric of the UV resistant compound.

Flexibility

Flexibility was determined by measurement of bending length of the fabric in both the warp and filling directions. ASTM method D 1388, Stiffness of Fabrics, Option A-Cantilever Method, was used. Results indicate no consistency in bending length measurements among the several samples. Explanation of the differences observed will require further examination.

Table 1

Phase II Fabric Identification

Sample No.	% Blancophor AW	% Tinuvin P	% Oxanilide
109-68-D Control	0	0	0
109-68-A Blank dyed	0	0	0
109-68-E	33	33	33
109-68-F	15	50	15
109-68-C	0	50	33
109-68-B	0	50	0

Table 2. Properties of Experimentally-Treated Nomex Fabrics

Property	109-68-E	109-68-C	109-68-A	109-68-F	109-68-B	109-68-D
Warp Ends per Inch	63.2	62.8	62.0	62.6	63.0	62.2
Filling Picks per Inch	49.0	49.0	48.8	49.0	49.0	48.4
Weight, oz/sq.yd.	7.23	7.09	6.42	7.16	7.46	6.27
Thickness, inch	.012	.012	.010	.011	.011	.009
Flexibility: Bending Length, inches: Warp	4.77	4.10	3.53	4.56	4.40	3.23
Fill	7.07	3.44	3.55	5.70	3.82	4.20
Air Permeability, cu.ft./min.sq.ft.	3.2	2.6	1.7	1.9	2.2	2.4
Breaking Strength, lbs.;Warp	247	241	241	254	219	242
Breaking Strength, lbs.;Fill	189	176	177	185	186	170
Abrasion Resistance:						
Breaking Strength,lbs,Warp	197	227	191	212	232	88
Breaking Strength Retained	79	94	79	84	106	36
Breaking Strength,lbs,Fill	179	189	145	190	179	64
Percent Strength Retained	95	107	82	103	96	38

Air Permeability

Air permeability was measured by the Frazier air permeability tester according to ASTM method D 737. The results indicate very high resistance to air passage through the fabric for all of the samples.

Breaking Strength

Breaking strength was measured according to ASTM method D 1682, 1-inch ravelled strip test. Filling strength of all samples was approximately the same, while warp strength of sample B was lower than that of the other samples.

Abrasion Resistance

This property was measured following ASTM method D 1175, flexing and abrasion method. Specimens 1 1/2" x 10" were ravelled to a width of 1 inch and abraded for 900 cycles with a tension load of 4 pounds and a head load of 1 pound. Strength of the abraded specimens was measured according to ASTM method D 1682. Percent breaking strength retained is shown in Table I and indicates that all of the treatments, including the blank dyeing, improved the abrasion resistance.

Results of the warp ends and picks per inch indicate that little dimensional change occurred during the treatment. The weight measurements show a 13 to 19% increase in weight as a result of treatment. From the appearance of the fabric it is probable that at least part of this weight increase is due to chemicals on the fabric surface which were not completely removed by the after-scouring step. Fabric flexibility was decreased somewhat as a result of the treatment.

One result which was not expected was the increase in abrasion resistance observed for the treated fabrics and the blank-dyed fabric. It is apparant that the dyeing operation has a very beneficial effect on abrasion properties and may be due to either lubrication of the fabric by carrier components or to changes due to thermal treatment during the process.

III. Flammability of Treated Samples

Treated, control and blank-dyed samples were tested in accordance with DOC-FF-3-71. Measurement of after-flame times, afterglow times and char lengths are given in Table 3. Afterglow times were comparable for all the samples tested and with the exception of sample 109-68-E, the char lengths were similar. Greater variation was observed in the afterflame times. Samples 109-68-E, and 109-68-C appear to have higher afterflame times. Since samples 109-68-E and 109-68-C both have 33% Oxanilide, this component of the treatment system may have an adverse effect on flammability. Reduction in the level of oxanilide in the treatment selected for Phase III should be considered as this appears to be the least effective component in improving the UV stability of Nomex.

IV. New Additive Addition Procedures

Samples for Phase II were prepared in a pressure jig dyeing machine. Due to the low agitation of treatment bath in the jig machine, the treatment chemicals did not remain suspended throughout the treatment cycle.

Discussions of this problem with the carrier manufacturer led to the suggestion that a more highly emulsified carrier might be desirable for pressure jig dyeing. An experimental carrier was formulated for use in the jig machine and a sample prepared with 33% of all these treatment chemicals in the dyebath. This sample is identified as 109-68-G. A comparison of the UV resistance of Sample 109-68-G and the comparable Phase II sample 109-68-E is shown in Table 4. The results indicate that the experimental carrier is somewhat less effective than the original carrier.

Jet dyeing has also been investigated as a means of treating Nomex fabric. A sample of fabric 12 inches by 30 feet was treated in a mini-jet

Table 3

Results of Vertical Flame Test on
Control, Treated, and Blank-Dyed Fabrics

Sample	Afterflame Time (sec.)	Afterglow Time (sec.)	Charlength
109-68-D warp	4.4	0.9	1.5
109-68-D filling	3.8	4.5	1.4
109-68-A warp	4.1	0.0	1.4
109-68-A filling	3.5	0.2	1.2
109-68-E warp	9.8	0.0	3.3
109-68-E filling	10.8	0.0	4.8
109-68-F warp	2.6	0.8	1.0
109-68-F filling	3.8	0.0	1.6
109-68-C warp	14.1	0.0	2.1
109-68-C filling	15.9	0.0	1.4
109-68-B warp	8.1	0.0	2.5
109-68-B filling	2.1	0.0	0.9

Table 4

UV Stability of Nomex Treated Using Experimental Carrier

Tensile Strength

Sample	0 hrs	50 hrs	100 hrs	150 hrs	200 hrs.
109-68-E	247	193	180	186	199
109-68-G	245	210	174	161	152

Elongation

Sample	0 hrs	50 hrs	100 hrs	150 hrs	200 hrs.
109-68-E	57	30	27	28	29
109-68-G	58	32	29	27	25

dyeing machine at the Celenese Laboratory in Charlotte, North Carolina. The treatment bath contained 33% Blancophor AW, 15% Tinuvin P and 7% Oxanilide. Results of testing of this sample (109-68-H) compared to the two best samples from Phase II (109-68-E and 109-68-F) are shown in Table 5. The 73% retention of tensile strength and 54% retention of elongation after 150 hours exposure to the carbon-arc are remarkable good considering that the weight pick-up in jet dyeing was only 5.42% (compared to 15.3% for sample 109-68-E and 14.2% for 109-68-F). Jet dyeing should be given serious consideration as the treatment technique selected for Phase III.

V. Technical Review Meeting

A meeting is planned for December 8 to review progress of Phase II and to plan Phase III of the project.

VI. Future Work

Major effort next month will be directed toward preparation for Phase III.

VII. Budget

The funds budgeted and either expended or allocated for the first seventeen months are shown on the attached graph.

Table 5

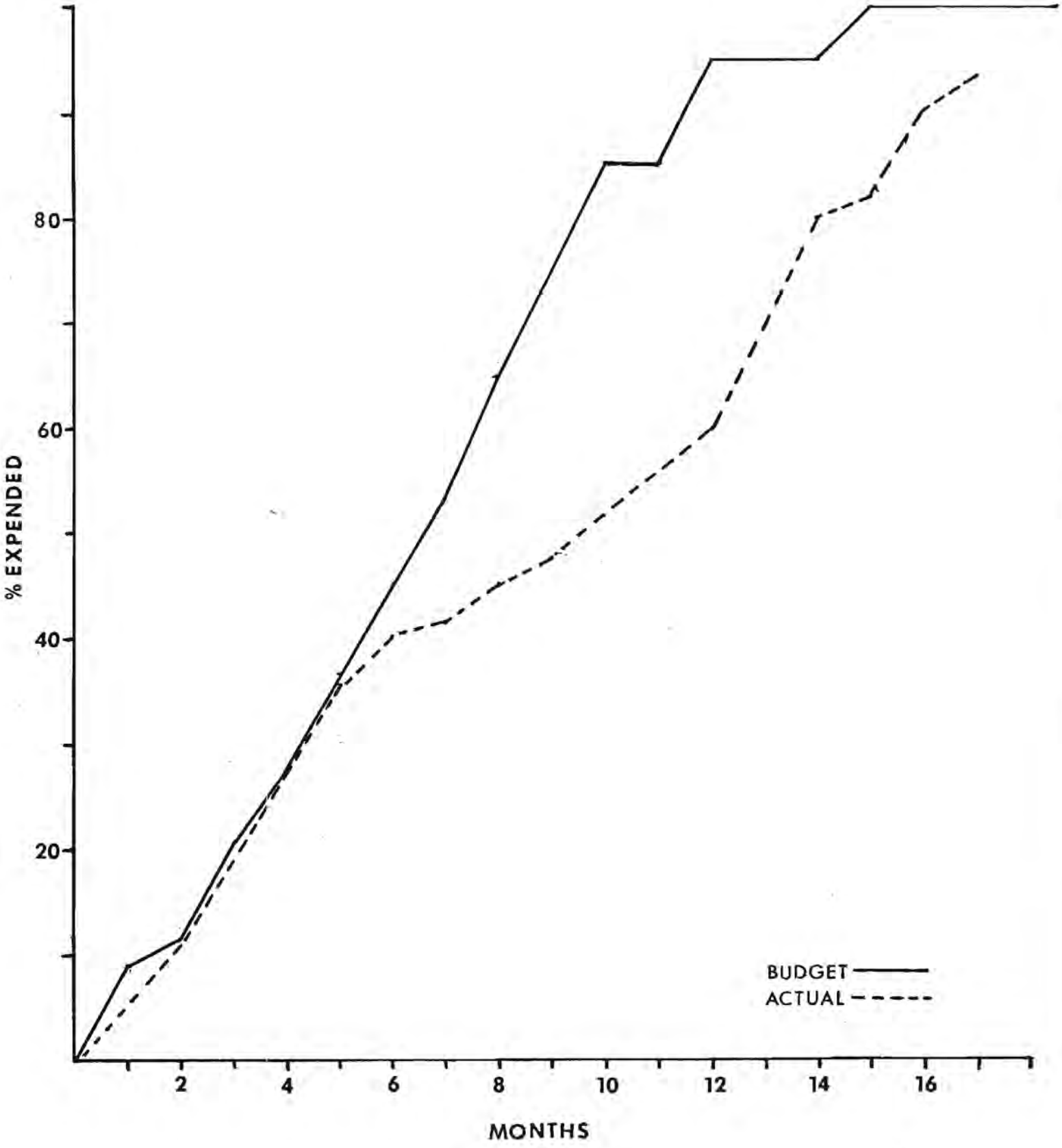
Comparison of Nomex Samples Treated
in a Jet and Jig Dyeing Machine

Tensile Strength

Sample	0 hrs	50 hrs	100 hrs	150 hrs	200 hrs
109-68-E	247	193	180	186	199
109-68-F	254	197	146	133	149
109-68-H	229	167	157	167	161

Elongation

Sample	0 hrs	50 hrs	100 hrs	150 hrs	200 hrs
109-68-E	57	30	27	28	29
109-68-F	63	28	28	27	33
109-68-H	63	37	34	34	31


80
60
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% EXPENDED
BUDGET
ACTUAL
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14
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MONTHS

C-27-623

MIL- (USAF)

MILITARY SPECIFICATIONS

FABRIC, NOMEX, TREATMENT FOR UV STABILITY

1. SCOPE

1.1 Scope. This specification covers requirements for treating Nomex fabric and webbing to reduce degradation by UV radiation.

2. APPLICABLE DOCUMENTS

2.1 The following documents of the issue in effect on date of invitation for bids form a part of this specification to the extent specified herein:

SPECIFICATIONS

Federal

MIL-C-38351A	Cloth, Parachute, Nylon, Aromatic, Nonmelting
MIL-W-38283A	Webbing, Textile, Aromatic Polyamide, Nonmelting

STANDARDS

Federal

Fed Std No. 191 Textile Test Methods

PUBLICATIONS

AFML-TR- Protection of Nomex from Ultraviolet Degradation

(Copies of specification, standards, drawings, and publications required by suppliers in connection with specific procurement functions shall be obtained from the procuring activity or as directed by the contracting officer.)

3. REQUIREMENTS

3.1 Equipment. High pressure jet dyeing machine capable of operating at 270°F and having sufficient capacity to permit a 25:1 liquor ratio (weight of treatment bath to weight of fabric treated). Tenter frame for open width drying of fabric at 300°F.

3.2 Materials

Blancophor AW	(GAF Corporation)
Tinuvin P	(Ciba-Geigy)
Oxanilide	(Eastman Organic Chemicals)
Chemocarrier FPN	(Tanatex Chemical Corporation)
Merpol LFH	(DuPont)

3.3 Procedures. Fabric is loaded in a jet dyeing machine and the machine filled with water to give a 25:1 liquor ratio. The bath is heated to 190°F (at 3°F/minute) and the treatment chemicals (Blancophor AW-33% owf, Tinuvin P - 33% owf, oxanilide-5% owf) dispersed in sufficient Chemocarrier FPN to give 0.05 gallon of carrier per gallon of treatment bath are added. The temperature is raised to 270°F (3°F/minute) and held at this temperature for 2 hours. The bath is discharged and the fabric scoured twice at 160°F in 1% owf Merpol LFH. After thorough rinsing the fabric is dried at a minimum of 250°F.

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for inspection. Unless otherwise specified in the contract or purchase order, the supplier is responsible for the performance of all inspection requirements as specified herein. Except as other specified in the contract or order, the supplier may use his own or any other facilities suitable for the performance of the inspection requirements specified herein, unless disapproved by the Government. The Government reserves the right to perform any of the inspections set forth in the specification where such inspections are deemed necessary to assure supplies and services conform to prescribed requirements.

4.2 Monitoring Procedures for Equipment. Machines for treating the fabric shall be equipped with a recorder to gives a permanent record of the temperature versus time during the treatment process.

4.3 Monitoring Procedures for Materials. Acceptance tests shall consist of the following for each lot of fabric treated:

(a) Overall examination
(b) Physical properties
(c) Resistance to UV degradation

4.3.1 Overall examination. Each roll in the sample shall be examined on the face side only. When the total yardage in the roll does not exceed 100 yards, the entire yardage of the roll shall be examined. When the total yardage in the roll exceeds 100 yards, only 100 yards shall be examined. The sample size shall be in accordance with the following:

Lot Size (yards)	Sample Size (Rolls)
3200 or less	8
3201 up to and including 1,000	13
10,001 and over	20

Each defect listed below shall be counted no more than once in each roll examined.

Defects

Objectionable odor
Unclean throughout
Uneven shading, spottiness

4.3.2 Physical Properties. Each roll in the test sample as defined in 4.3.1 above shall be tested for the properties indicated in Table 1. Properties of the treated fabric shall be within the limits indicated in Table 1 when compared with fabric before treatment.

4.3.3 Resistance to UV degradation. Each roll in the test sample as defined in 4.3.1 above shall be tested for resistance to UV degradation as outlined in 4.5.2. Treated samples shall retain greater than 75% of the unexposed breaking strength after 150 hours exposure to the Sunshine Arc Fade-Ometer.

4.5 Test Methods

4.5.1 Physical Properties. Test methods for physical properties are given in Table 1.

4.5.2 Resistance to UV Degradation. Samples before and after treatment shall be tested for UV degradation in accordance with Fed Std 191 Method 5804 except that the water spray shall be turned off. Breaking strength in the warp direction shall be determined initially and after 150 hours exposure in accordance with Fed Std 191 Method 5104.

6. NOTES

6.1 Intended Use. The treatment process described in this specification is intended for use on fabrics for application in parachutes and parachute accessories.

Table 1 Test Methods

Characteristic	Requirement	Test Method of Fed Std. No. 191
Yarns-per-inch	± 10% of untreated	5050
Thickness	± 10% of untreated	5030
Weight	+ 10% to 20% of untreated	5041
Breaking Strength	± 10% of untreated	5104

E-27-623

MIL- (USAF)

MILITARY SPECIFICATIONS

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SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
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4. TITLE *(and Subtitle)* PROTECTION OF NOMEX FROM ULTRAVIOLET DEGRADATION		5. TYPE OF REPORT & PERIOD COVERED 1 July 1974 - 28 Feb. 1976 6. PERFORMING ORG. REPORT NUMBER E-27-623
7. AUTHOR(s) Wayne C. Tincher Walter C. Carter David R. Gentry		8. CONTRACT OR GRANT NUMBER(s) F33657-74-C-0716
9. PERFORMING ORGANIZATION NAME AND ADDRESS Georgia Institute of Technology School of Textile Engineering Atlanta, Georgia 30332		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS FY7615-74-01251
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Nomex, Aramid, aromatic polyamide, UV, degradation, stabilizer, Blancophor AW, Tinuvin P, oxanilide, exposure, strength, elongation, fabric, webbing

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

A stabilizer system has been developed for Nomex fabrics and webbing to reduce UV degradation. Treated fabric samples retain greater than 75% of the initial tensile strength after 150 hours exposure to the Sunshine Arc Fade-Ometer compared to less than 50% retention for untreated samples. The treatment system contains Blancophor AW, Tinuvin P, and oxanilide and may be applied to fabrics from an aqueous emulsion at 265°F by means of an acetophenone based carrier.

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SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

PREFACE

This report was prepared by the School of Textile Engineering, Georgia Institute of Technology, Atlanta, Georgia under U.S. Government Contract No. F33657-75-C-0716. It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command with Mr. Walter Gloor acting as project engineer.

Dr. Wayne C. Tincher of the Georgia Institute of Technology was the principal investigator for the project. Dr. Walter C. Carter and Dr. David Gentry were responsible for certain phases of the project. The laboratory studies were carried out by Ms. Sandra K. Henson and Mr. Mathew Sikorski.

The authors wish to express their appreciation to the E. I. du Pont de Nemours Company and the Ciba-Geigy Company for many helpful discussions and suggestions during the course of the work and to Celanese Corporation, Monsanto Textiles Company, and Hoechst Company for use of laboratory facilities for production of treated Nomex fabric and webbing samples.

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LIST OF TABLES

LIST OF TABLES (cont'd.)

SECTION I

SUMMARY

A. Program Objective and Scope

The objective of this work was the development and evaluation of a treatment system for improvement in the resistance of Nomex fiber and fabrics to UV degradation. Specifically, a system was sought which would yield 75% retention of the tensile strength of Nomex fabrics after 150 hours exposure in the Atlas Sunshine Carbon Arc Fade-Ometer. To achieve this objective, a survey was conducted of all literature and manufacturer's data related to Nomex UV stabilization. Techniques were developed for incorporating stabilizers in Nomex fiber and a number of potential stabilizers (UV absorbers, free radical scavengers, quenching agents) were screened for effectiveness in reducing Nomex UV degradation. Additives which showed promise were tested at various levels and in combination to determine effective concentrations and to develop the best possible stabilizer system. Four fabric samples were treated with the most promising system and evaluated. The most effective system was used to treat 200 yards of Nomex fabric (MIL-C-38351,Type II,Class 1) and 100 yards of Nomex webbing (MIL-W-38283,Type XII). The treated fabric and webbing samples retained greater than 80% of the original tensile strength after exposure for 150 hours in the Atlas Sunshine Carbon Arc Fade-Ometer.

B. Conclusions

Technical literature and manufacturers' data contain little information useful in selecting stabilizers to improve Nomex light stability. Most of the commonly used stabilizers for fibers and plastics are ineffective or even detrimental in degradation of Nomex by UV light. Three compounds (Blancophor AW, Tinuvin P, Oxanilide) were found which reduced the loss in tensile strength and elongation of Nomex fiber during UV exposure.

A modified "dyeing technique" has been developed which permits incorporation of stabilizers in Type 430 continuous filament Nomex. The procedure requires treatment of the fiber at high temperature (265°C) in the presence of large quantities (40 g/l) of a carrier (Tanatex Chemocarrier FPN).

A stabilizer system composed of 33% (owf) Blancophor AW, 33% (owf) Tinuvin P and 5% (owf) Oxanilide proved to be very effective in reducing UV degradation of Nomex. Nomex fabric samples treated with this system showed greater than 80% retention of tensile strength after 150 hours exposure to the Atlas Sunshine Carbon Arc Fade-Ometer compared to less than 50% retention of tensile strength for identical, untreated Nomex fabrics. Similar improvements were observed on exposure of the fabric to the Xenon Arc Fade-Ometer.

C. Recommendation

Attempts should be made to optimized the stabilizer system to achieve more economical treatment. It may be possible to reduce the quantity of stabilizers used significantly with little or no reduction in UV stability.

A "standing bath" solvent treatment technique would probably be preferred to the modified dyeing procedure used in the present work. Such a system could substantially reduce the cost of treating Nomex to improve UV stability.

More extensive outdoor exposure studies should be conducted on treated Nomex samples for comparison with the data obtained by carbon arc and xenon arc exposure.

SECTION II

SELECTION AND EVALUATION OF STABILIZERS

A. Introduction

Heat resistant and nonflammable fibrous materials composed of aromatic or aromatic/heterocyclic polymeric systems are components of a number of Air Force end items including uniforms, flight and protective clothing, life support equipment and decelerator materials. Although these materials show considerable resistance to loss of physical properties when exposed to high temperatures (such as fuel fires), they are generally deficient in resistance to UV degradation. This susceptibility to UV degradation is a major factor in replacement cost and reliability of air force materials. For example, operational experience has shown that degradation due to solar radiation is largely responsible for frequent replacement of parachute pack fabrics [1].

Studies on stabilization of heat resistant fibrous materials to UV degradation have not yielded practical procedures for improvement of the service life of these materials. It was evident that the degradation process was complex and simple single component additives were not likely to give adequate stability. Synergistic stabilizer systems containing a number of carefully selected components were expected to be required to meet target objectives.

An additional problem is encountered in attempting to add stabilizers to Nomex fiber or fabric. After extrusion and drawing aromatic polyamide fibers tend to be intractable and diffusion of materials into the fiber is difficult to achieve. Significant effort was required to develop innovative techniques for addition of stabilizer systems to the fiber and insure their permanency. It was further essential that the selected stabilizer system (and techniques for incorporation in or on the fiber) not adversely affect desirable mechanical or thermal properties of the Nomex fabrics.

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[1] May, Donald R., Jr. and Ross, Jack H., Accelerated Weathering of Polyamides, Aromatic Polyamides, and Polybenzimidozole Fabrics, AFML-TR-72-137, October 1972.

B. UV Degradation of Nomex

The susceptibility of aromatic polyamides (aramides) to UV degradation has been well documented [1-4]; however, there is little information available in the literature on the mechanism of UV degradation of these materials. Nomex absorbs UV radiation beginning at approximately 390 nanometers (nm) and extending into the near UV with a peak at approximately 360 nm. This absorption is responsible for both the yellowing of the fiber and the loss in tensile strength [2]. Similar results have been reported on other aromatic polyamides. In this respect the aramides differ significantly from other common polymeric systems. Aliphatic polyamides, for example, are degraded by light in the region near 290 nm [5]. Sunlight is much richer in radiation at 360 nm than at 290 nm and this fact undoubtedly accounts for the much greater susceptibility of aramides to degradation by solar radiation.

Some attempts have been reported to find UV screening agents for improvement of Nomex light stability [3]. These studies have not led to the discovery of viable systems for practical application.

Other information on the fundamental aspects of aramide UV degradation such as -- identity and nature of the absorbing species, structure of the excited state, mechanism of the chemical reactions responsible for loss of

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[2] Ross, Jack H. and Daukays, Mary Ann, Mechanical Properties of Woven Forms of Three Polyaromatic Fibers After Ultraviolet Exposure. AFML-TR-67-415, April 1968.

[3] Karsny, J.F. and Schwartz, A.M., Nomex Ultraviolet Inhibitors, ASD-TR-72-104, August, 1972.

[4] Johnson, L.D., Tincher, W.C., and Bash, H.C., "Photodegradation Wavelength Dependence of Thermally Resistant Organic Polymers", J. Applied Polymer Sci., 13, 1825 (1969).

[5] Taylor, H.A., Tincher and Hamner, W.F., "Photodegradation of Nylon 66. I. Phototendering by TiO_2", J. Applied Polymer Sci., 14, 141 (1970).

mechanical properties, possible role of water and/or oxygen in the degradation -- is not available in the literature. These important basic aspects of aramide UV degradation are part of on-going graduate student research at the Georgia Institute of Technology. Some preliminary results of this work are given in Appendix C.

C. Principles of Stabilizer Selection

In the absence of detailed information on aramide photodegradation, guidance for selection of stabilizer systems must be found in the recent advances in knowledge of the nature and behavior of electronic excited states and in understanding of photochemical reactions in polymeric systems. Ultraviolet degradation of these materials can generally be divided into three phases -- absorption of a photon, production of an initial excited species, and subsequent chemical reactions of the excited molecules. Stabilizers which are effective in reducing photochemical degradation must prevent or significantly reduce one or more of these steps.

1. Photon Absorption

One class of stabilizers compete with the polymer substrate for available photons (screening agents). These materials must have very strong absorption in the same region of the spectrum as the polymeric material. In the case of Nomex these compounds should absorb in the region from 300 to 390 nm. The usual screening agents used for other polymers generally absorb at shorter wavelengths. Quite different materials will be required for Nomex stabilization. In addition the screening agent must not degrade itself on absorption of UV energy.

2. Initial Excited Species

Most polymeric systems degrade by initial production of an excited species (e.g., triplet state, free radical, charge transfer complex, etc.). A second approach to stabilization is the inclusion of a compound capable of reacting with, and therefore deactivating the excited species. Stabilizers for some polymers, particularly aliphatic polyamides (copper and manganese compounds) apparently react in this way.

3. Degradative chemical reactions

Most polymer systems degrade by a free radical-peroxide-hydroperoxide mechanism summarized by the following reactions:

polymer• + O_2 → polymer -0-0• (1)

polymer-0-0• + H-polymer → polymer-00H + polymer• (2)

polymer-00H → polymer-0• + •0H (3)

polymer-0• → chain scission (4)

In reaction (1) a free radical (denoted by the dot indicating an unpaired electron) produced in a polymer molecule by the initial excited species reacts with oxygen in the air to give a peroxide radical. The peroxide radical abstracts a hydrogen atom from an adjacent polymer molecule to give a hydroperoxide and a new polymer free radical (reaction 2). The hydroperoxide then cleaves to give an oxy radical and a hydroxyl radical (reaction 3). The oxy radical usually undergoes a polymer chain scission giving a reduction in molecular weight and a loss in mechanical properties (reaction 4). In this series of reactions two new radicals have been produced (polymer• in reaction 2 and •0H in reaction 3) to continue the free radical chain reaction sequence. Most successful stabilization systems for polymers contain at least one component capable of interrupting this series of chain reactions. These materials either react with free radicals to produce stable products (radical scavenger) or are capable of decomposing peroxides in a nondestructive manner.

Successful systems for polymer stabilization generally contain several components which are capable of intercepting the degradation sequence at several different points. For example, a typical system might include a screening agent to compete with the polymer for photons, a metal ion for preferential reaction with excited species, and a radical scavenger to remove free radicals from the system. Synergistic effects between these types of stabiliers are important in development of a successful stabilizer system.

C. Stabilizers Selected for Screening

1. Literature Survey

A major objective of the literature survey was to identify materials that had been recommended as UV stabilizers for Nomex. A detailed discussion of the literature survey is given in Appendix A. In the important area of UV stabilizers 13 references were discovered. The reported stabilizers were primarily UV screening agents. The literature, therefore, provided little guidance in selection of compounds for Nomex stabilization. Twelve references were found that discussed the mechanism of radiation and UV degradation of Nomex and other aramids. These references were useful in selection of some materials for screening studies.

2. Survey of Manufacturers

a. E. I. duPont de Nemours & Company

Discussions of the Nomex UV stability problems were held with Dr. Calvin J. Cruz, Supervisor Nomex Technical Service and Dr. Bob Thomas, Jackson Laboratory. DuPont's major interest has been in the dye lightfastness of Nomex because this property has limited application of Nomex in commercial aircraft interiors.

At the present time DuPont is adding a UV screening agent to both colorsealed sage green (Type 433) and olive green (Type 432) Nomex. There is little evidence that the additive is effective but they have been reluctant to change the production process by removing it.

The Jackson Laboratory has conducted fundamental studies on the mechanism of degradation of dyes on Nomex. Although the work related more directly to dye light-fastness, the conclusions and results have important implications in selection of UV stabilizers. Some important conclusions were:

(1) Photodegradation is characteristic of all aromatic polyamides. Extensive structural modifications do not prevent degradation.

(2) Nomex is a very strong absorber between 350 and 400 nm. The quantum efficiency for degradation is low (10^{-4} to 10^{-5}). The process is a non-chain reaction and it is not autocatalytic.

(3) Oxygen is necessary for degradation. The uptake of oxygen is linear with time if light intensity is constant. Normal free radical scavengers and antioxidants are not effective stabilizers.

(4) UV screening agents are partially effective.

(5) A number of conventional mechanisms have been considered:
   (a) formation of aminobenzophenone (by Photo-Fries reaction)
   (b) Photohydrolysis and oxidation
   (c) Formation of phenazine
   (d) Tautomeric shift involving cyclization across C=N bonds

None of these mechanisms is completely satisfactory. The possibility of oxygen in the first excited singlet state being important in the mechanism has also been considered. Again the evidence was not conclusive.

The DuPont work suggests that, with the exception of UV screening agents, conventional light stabilizer systems may not be effective on Nomex.

b. Ciba-Geigy

Ciba-Geigy appeared to be aware of the Nomex light stability problem and has conducted some work in the area. Several Ciba-Geigy materials in the Tinuvin series of UV screening agents and the Irganox series of antioxidants were suggested for stabilization of Nomex. An experimental material GI-10-460 (an aromatic diamide of oxalic acid) which is reported to be a light stabilizer for Nomex was also suggested for inclusion in the screening program.

c. Other Manufacturers of Stabilizer Candidates

In addition to DuPont and Ciba-Geigy, conversations were held with representatives of American Cyanamid, Sandoz, Eastman Chemical Products, and Ferro Corporation. The Nomex stability problem was discussed and each company sent samples of materials they manufactured or had under development which might provide UV protection for Nomex. Stabilizer candidates for screening were selected from these materials based on their structures and likely mode of action in interrupting the Nomex degradation mechanism.

3. Stabilizers Screened

The specific stabilizers selected for screening studies are shown in Table 1. The stabilizers fall into four major groups -- UV absorbers, antioxidants, quenchers and/or radical scavengers, and other potential stabilizers which function by mechanisms other than the typical UV stabilizers.

a. UV Absorbers

UV screening agents improve the light stability of fibers and fabrics by competing with the substrate for the photons responsible for degradation. To be effective, screening agents must have two important characteristics. First, they must have strong absorption in the same region of electromagnetic radiation as the substrate. Second, the screening agent must have means of dissipating the excess energy obtained by absorption of electromagnetic radiation without degrading itself or stimulating the degradation of the substrate. These are rather stringent requirements and only a few chemical structures can function as UV screening agents.

The absorption spectrum of Nomex in the near UV and visible region which is responsible for Nomex photodegradation is shown in Figure 1. Compared to most fiber-forming polymers the absorption of Nomex is much nearer the visible region of the spectrum. Sunlight has a significant quantity of energy in this region which may account for the sensitivity of Nomex to UV degradation. Unfortunately, most UV screeening agents designed for improving stability of polymeric materials absorb strongly further in the UV than Nomex. The overlap between screener absorption bands and the Nomex degradation band is not as large as desirable for maximum efficiency.

One class of materials which do have strong absorption bands in the same region of the spectrum as Nomex is the fluorescent brightening agents. An absorption spectrum for a typical brightener is shown in Figure 2. A comparison of Figure 2 and Figure 1 indicates that fluorescent brighteners should be able to compete effectively with Nomex for the photons responsible for degradation. In addition, the brightening agents can lose excess energy by fluorescence and can therefore show sufficient stability to be of interest as UV screening agents.

Five optical brighteners were selected for investigation. These materials are given in Table 1. All are

Table 1

POTENTIAL STABILIZERS SCREENED FOR IMPROVEMENT IN NOMEX UV STABILITY

UV Absorbers	Antioxidants
Lencophor EFR	Irganox 1035
Uvitex NFW	Plastinox 1735
Uvitex WGS	Irganox 1010
Blancophor AW	Irganox 1098
Uvitex RBNAD	CHI-316
Tinuvin P	
Tinuvin 327	
Tinuvin 770	
Eastman Inhibitor RMB	

Quenchers	Other
Irgastab 2002	Oxanilide
Zetax	beta-oxynalplthoic acid
GI-10-460	thiourea-urea
CHA-1058	colloidal sulfur
Nickel dibutyldithiocarbomate	
Ferro AM-105	

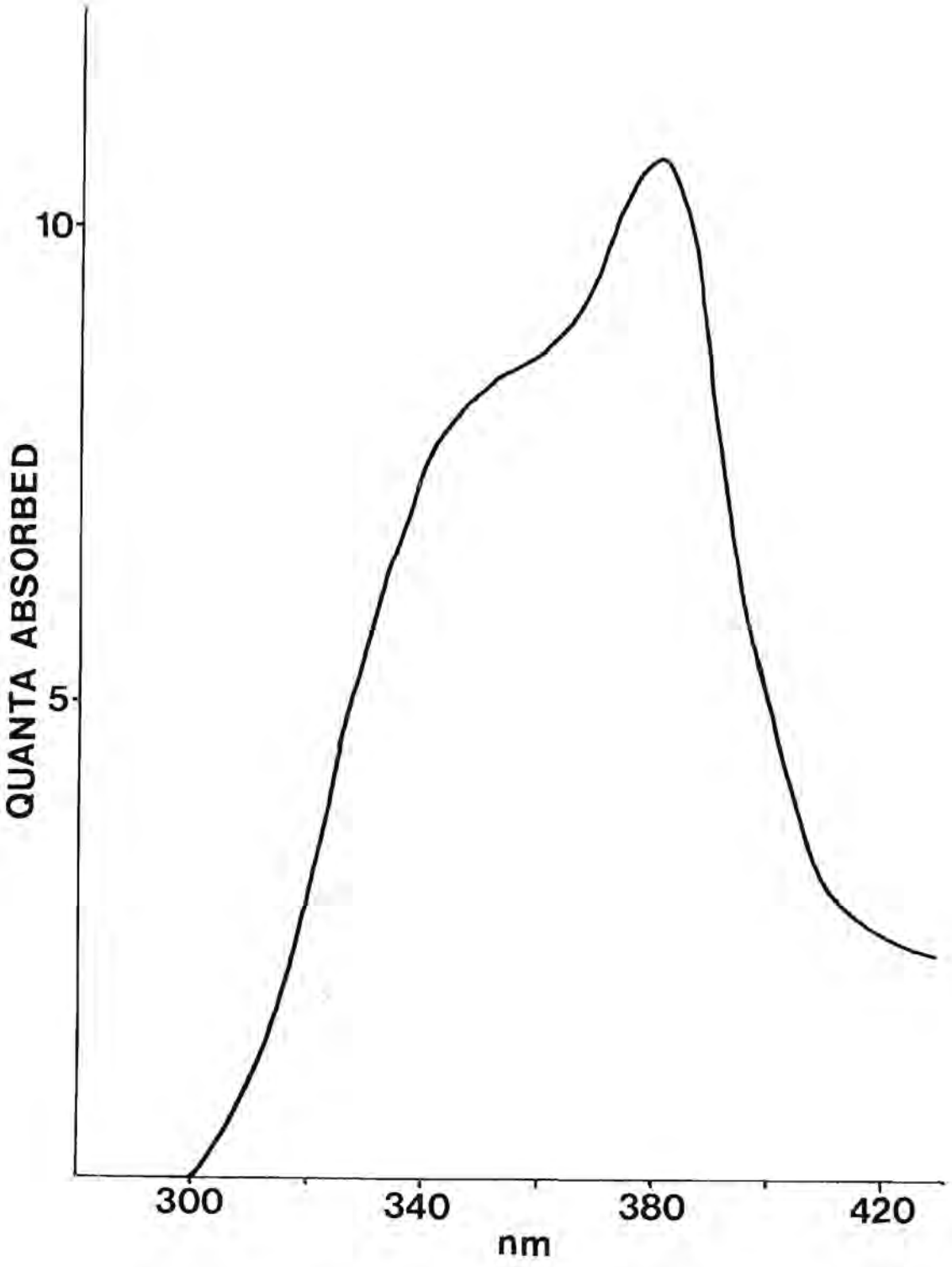

Figure 1. Absorption spectrum of Nomex

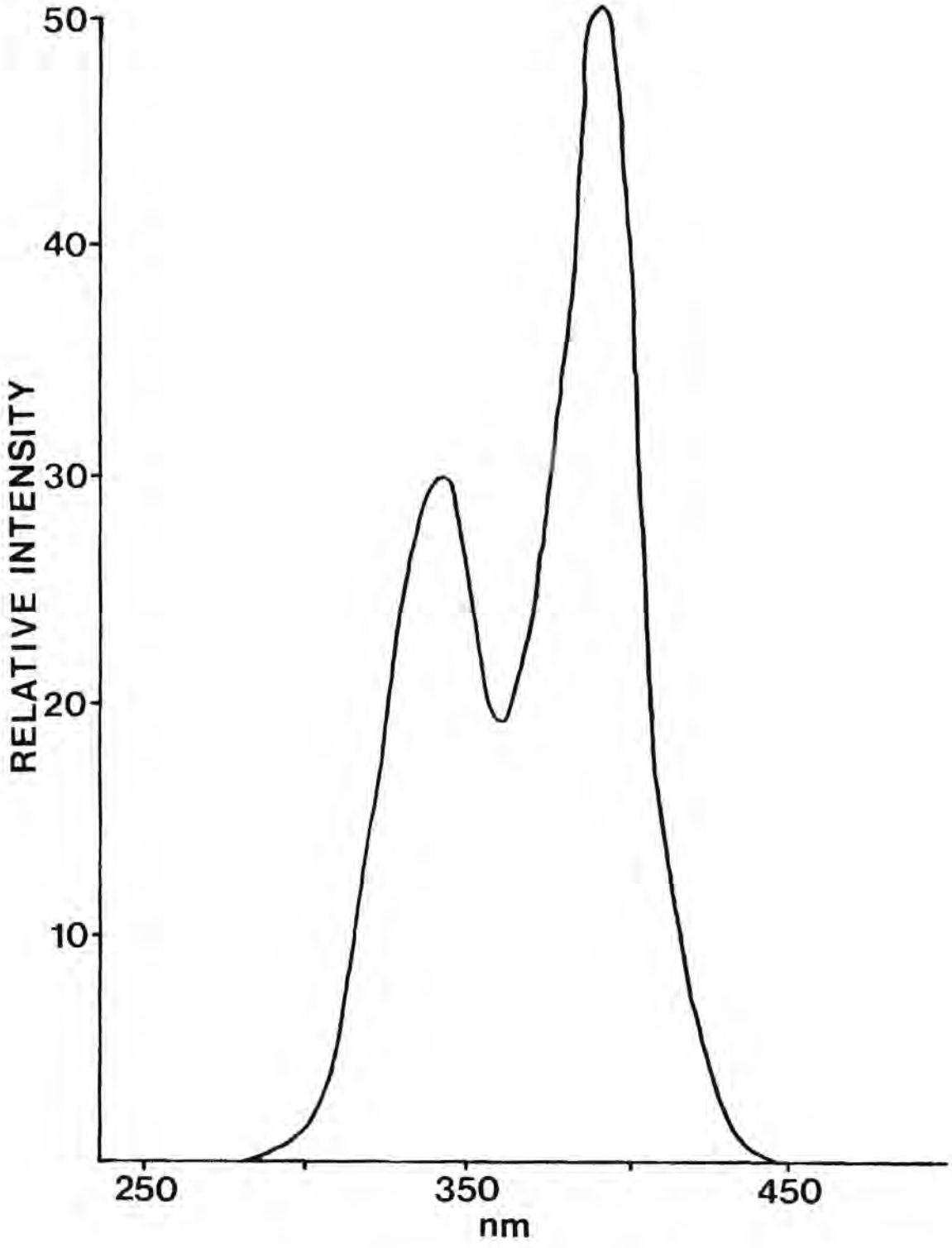

Figure 2. Absorption spectrum of Uvitex RBNAD

optical brighteners recommended for use on polyamides and are reported to be among the more stable optical brighteners recommended for use on polyamides.

In addition to the optical brighteners investigated, studies were also conducted using conventional UV screening agents (absorbers). Because of their excellent performance in a wide range of polymers and reports in the literature on their stabilizing effects in Nomex, The Tinuvin series of screening agents was selected for study. The Tinuvins are substituted hydroxphenyl benzotriazoles which have strong absorption in the near UV and have excellent stability to UV degradation. Tinuvin P and Tinuvin 327 were the specific compounds used in this investigation.

In addition one substituted Triazine type UV absorber, Cyasorb UV 800 (American Cyanamid) was also included in the study.

b. Antioxidants

The hindered phenols have been one of the most effective groups of compounds that act as antioxidants. The Irganox compounds are hindered phenols with amide, ester, and thioglyoxal substitutent groups.

c. Radical Scavengers/Excited State Quenchers

Organometallic compounds and metallic salts have been effective in stabilizing aliphatic amides, probably by reaction with either free radicals or with excited species produced by the absorption of light. The compounds of this type shown in Table 1 have been effective in stabilizing other polymers against UV degradation.

A number of commercial quenching agents as well as several experimental materials were included in the screening studies.

d. Other Potential Stabilizers

A number of other compounds were investigated which do not fall in the usual categories of UV stabilizers. It has been reported that sulfur dyes have a light stabilizing action on aromatic polyamides and thiourea has been suggested as a light stabilizer for dyes. An attempt has been made to incorporate this material in Nomex by a padding-thermofixation process (200°C).

Oxidation of thiourea results in the formation of compounds possessing the disulfide link and also elemental sulfur, both of which may act to stabilizer the fibers.

During the course of the screening studies, some results were obtained which suggested that amine end groups might be related to the degradation of Nomex. Beta-oxynapthoic acid was added in an attempt to remove amine end groups by chemical reaction.

One reference in the patent literature [6] suggested that oxanilide is a good stabilizer against UV degradation. Since this material is structurally similar to Nomex, oxanilide was included in the materials screened for effectiveness in Nomex stabilization.

D. Techniques for Addition of Stabilizers to Nomex

In order for a stabilizer to be effective, it must be incorporated in the fiber or in a resin used in finishing. Little is known concerning the incorporation of various materials in Nomex except what is available in the published dyeing technology. This information is confined to recommended procedures for the application of cationic dyes. Since the types of materials being considered as stabilizers include both ionic and non-ionic materials, initial studies included the application of selected dyes from several classes of dyes by techniques and under conditions recommended for cationic dyes to learn more concerning the relationship between structural features of dyes and their substantivity to and diffusion in the fiber. These experiments were carried out both in the presence and absence of a suitable plasticizer for the fiber to promote diffusion in the fiber. Based on the results obtained, stabilizers (UV screens, antioxidants, UV stabilizers, fluorescent brighteners) were applied to the fiber using conditions for their application which would be predicted to promote reasonable sorption and degree of fiber penetration.

In all of the literature concerning the dyeing of Nomex, high concentrations of dye carriers are required at dyeing temperatures higher than 212°F. Many carriers have been evaluated for the application of cationic

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[6] Luethi, C.; Biland, H. R.; Duennenberger, M.; "Bis(oxalic acid aromatic diamides) useful as ultraviolet stabilizers for polymers;" South African Patent 68:2,135; September 1968.

dyes [7]. Those recommended include benzaldehyde [8] for Nomex E8 (a fiber chemically modified for dyeing with cationic dyes) and acetophenone [9]. Recommendations for dyeing Nomex type 450 include the use of acetophenone (40 g/l) at a dyeing temperature of 250 F. Conversations with Dr. P. G. Noble and Richard Hunt of Tootal Limited, Manchester, England, revealed that they had successfully dyed Nomex with cationic dyes using benzyl alcohol. A British patent [10] which describes this process has been issued to Tootal. In their work it was discovered that important factors in the light stability of cationic dyes on Nomex were the purity of the dyes, and the type and purity of surfactants used for emulsification of the carrier.

DuPont makes no recommendation for the dyeing of Nomex type 430; however, they report that it has been dyed successfully following the teachings of U.S. Patent 3,771,949 [11]. This dyeing process is very complicated requiring pretreatments of the fiber with high boiling liquids such as ethylene glycol, propylene glycol, tetraethylene glycol, and their alkyl derivatives at temperatures of approximately 190°C followed by application of cationic dyes in solvent mixtures consisting typically of such solvents as dimethylacetamide, dimethylformamide, and dimethylsulfoxide.

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[7] Schumm, R.W. and Cruz, C.J.; "Dyeing and Finishing Nomex Nylon"; Textile Chemist and Colorists, 1, 388 (1969).

[8] Evans, B.A. and Schumm, R.W.; "Dyeing Nomex Type 450 Nylon"; Textile Chemists and Colorist, 2, 262 (1970).

[9] duPont Technical Information Bulletin N-249, June 1971.

[10] Easthope, E. and Noble, P.G.; "Improvements in the Dyeing of Textile Materials (Aromatic Polyamides)"; British Patent 1,277,434; June 1972.

[11] Hermes, J.; "Pretreatment and Dyeing of Shaped Articles Derived from Wholly Aromatic Polyamides"; U.S. Patent 3,771,949; November 1974.

Fabrics made from Nomex type 430 dyed using procedures recommended for Nomex type 450 are unsatisfactory due to streakiness and lack of penetration of the dye into the fiber. The following types of dyes have been applied to Nomex type 430 at 250°F using the carrier, benzyl alcohol, at concentrations up to 100 g/l:

Leveling acid
Neutral dyeing acid
Disperse
Cationic

In all cases, 5.0% dye based on fiber weight was used. Medium depths of shade were obtained with disperse, cationic, and neutral dyeing acid dyes when the concentration of carrier was 100 g/l. Propylene carbonate was ineffective as a carrier under the same dyeing conditions. The dyeing results with benzyl alcohol were convincing evidence that anionic, cationic, and non-ionic materials can be incorporated in the fiber.

Acetophenone is recommended by duPont as a carrier for dyeing Nomex 450. It was discovered that Chemocarrier FPN, a compounded carrier composition reported to be based on acetophenone (Tanatex Corporation), was effective in applying cationic and disperse dyes to Nomex. The concentration of the carrier required was 40 g/l at a dyeing temperature of 250-260°F.

Other materials which were investigated included salicylic acid and o-benzoic sulfimide. They were chosen because it was thought that they may be effective carriers due to the fact that they are both small molecules possessing high dipole moments. In addition, they are also capable of forming complexes with metal ions which could serve as stabilizers for Nomex. Dyeing studies using these materials showed that both materials provide some carrier action, salicylic acid being more effective than o-benzoic sulfimide.

Of all carriers investigated in the dyeing experiments, Chemocarrier FPN proved to be most effective for incorporation of dyes in Nomex. This carrier was used in all subsequent experiments in which stabilizer were incorporated in Nomex.

Potential stabilizers were applied to Nomex Type 433 Sage Green 200 denier, 100 filament yarn samples by procedures similar to those used for dyeing of Nomex fiber.

The fiber (2.5 grams) was wound loosely on a stainless steel wire flame and placed in stainless steel cans containing the treatment solution. Composition of the treatment bath was

2.5 grams stabilizer candidate
5.0 ml Chemocarrier FPN (Tanatex)
125 ml total volume of bath (50:1 liquor ratio)

The cans were sealed and placed in an Atlas High Temperature Launder-Ometer at room temperature. The temperature was raised to the treatment temperature (250°F for optical brighteners and 260°F for the UV absorbers) at 3 F per minute. The temperature was held at 250°F (or 260°F) for two hours followed by a 15 minute cooling cycle. The fiber samples were then removed and scoured in a bath containing

5.0% Merpol HC (o.w.f.)
6.0% $Na_4P_2O_7 \cdot 3 H_2O$ (o.w.f.)
125 ml total value of scouring bath
(50:1 liquor ratio)

The scouring was carried out at 180° F for 15 minutes followed by a thorough rinse.

A control sample (blank dyed sample) was prepared using the same procedure described above except that the optical brightener, UV absorber, or other stabilizers were omitted.

As noted earlier sulfur containing compounds and in particular sulfur dyes (containing disulfide bonds -S-S) have been reported to stabilize aromatic polyamides against UV degradation. Two techniques for in-situ production of sulfur containing compounds were employed - reaction between urea and thiourea and acid decomposition of soidum thiosulfate.

The treatments of Nomex with aqueous solutions of urea and thiourea were as follows:

1. Urea 100 g/l
2. Thiourea 100 g/l
3. Urea and thiourea, 50 g/l each

Skeins (2.5 g) of Nomex yarn, Type 430, were treated in 125 ml of these solutions at 250° F for two (2) hours followed by rinsing to remove superficially held urea and

thiourea. The treated yarns were then subjected to Fade-Ometer exposure.

An attempt was made to produce colloidal sulfur in Nomex by first treating the yarn in a solution of formic acid (40 g/l) at 250°F for 2 hrs. followed by a treatment with an aqueous solution of sodium thiosulfate (10 g/l) at 212°F for 15 minutes. It is known that this reaction produces collodidal sulfur.

For these preliminary screening studies, no attempt was made to obtain quantitative data on the quantity of stabilizers actually picked-up from the bath by the Nomex fiber. Fibers were examined under a UV light following the treatment with optical brighteners and it was apparent that substantial quantities of the brighteners had been incorporated in the fiber.

E. Exposure and Testing

Control samples, samples which had been blank dyed and samples containing UV screening agents were exposed to light from either a xenon-arc or carbon-arc in Atlas Fade-Ometers. Xenon-arc exposures were carried out in a Model F Fade-Ometer equipped with a preaged 2500 watt arc with IR absorbing inner and quartz outer filters. The Fade-Ometer was equipped with a humidity control unit and was operated at a black panel temperature of 150°F and a relative humidity of 50%. Samples were exposed up to 100 hours with specimens removed from the Fade-Ometer at 20 hour intervals.

Carbon-arc exposures were conducted in a Type W Weather-Ometer with twin enclosed carbon-arcs. Relative humidity was maintained at 50% and the black panel temperature at 150°F.

In each series of exposures, both control and "blank dyed" samples were exposed simultaneously with the treated specimens.

Breaking strength and elongation of yarns were tested with an Instron constant-rate-of-extension tester, following procedures described in ASTM method D 2256. Tests on control and irradiated yarns were made with a 5 inch gage length and an extension rate of 100 percent per minute. The time required to break is a function of gage length, extension rate, and breaking elongation. Since breaking elongation was expected to vary with level of irradiation,

time-to-break was not used as a criterion of testing as specified in the ASTM method. The 5-inch gage length was chosen to accommodate the relatively short yarn lengths exposed to the UV light source.

Because of the difficulty of securing the same tension in all the filaments and because of slippage in the clamps, erratic results are frequently obtained with zero-twist multifilament yarns unless a small amount of twist is inserted before testing. A twist of (110 $\pm$ 10 tpi)/$\sqrt{D}$, where D is the multifilament yarn denier, was used to overcome these problems.

Twenty tests were made on each sample. This level of testing was selected to provide a maximum error of $\pm$ 3 percent for strength and $\pm$ 5 percent for elongation of the control yarns. Variation in observed results of both of these properties was expected to increase with increased levels of irradiation. Consequently, the error in estimation of these properties measured on the exposed yarns was somewhat higher.

F. Results of Screening Studies

1. Exposure Studies on Untreated Nomex Samples

Samples of Nomex type 430 (white) were exposed to the carbon arc and xenon arc lamps in the Fade-Ometer for 100 hours. Tensile strength and elongation were determined at 20 hour intervals for the exposed samples. Results of these experiments are shown in Figures 3 and 4. It is apparent from these data that exposure to the carbon arc gives much more rapid deterioration in the properties of Nomex. The carbon arc has very intense bands of radiation between 350 and 425 nm. This intense output corresponds directly with the wavelengths of energy responsible for Nomex degradation. The carbon arc exposure is therefore probably more severe than outdoor exposure in degradation of Nomex. Xenon arc exposure probably compares more favorable with outdoor exposure. The results also clearly indicate that the fiber elongation is more severely affected than the tenacity on exposure to UV radiation.

Similar exposure studies were conducted on Nomex type 433 (sage green) yarns and the results are shown in Figures 5 and 6. It is apparent from these results that the rate of degradation of the type 430 (white) Nomex is much greater than rate for type 433 (sage green) for both exposure sources.

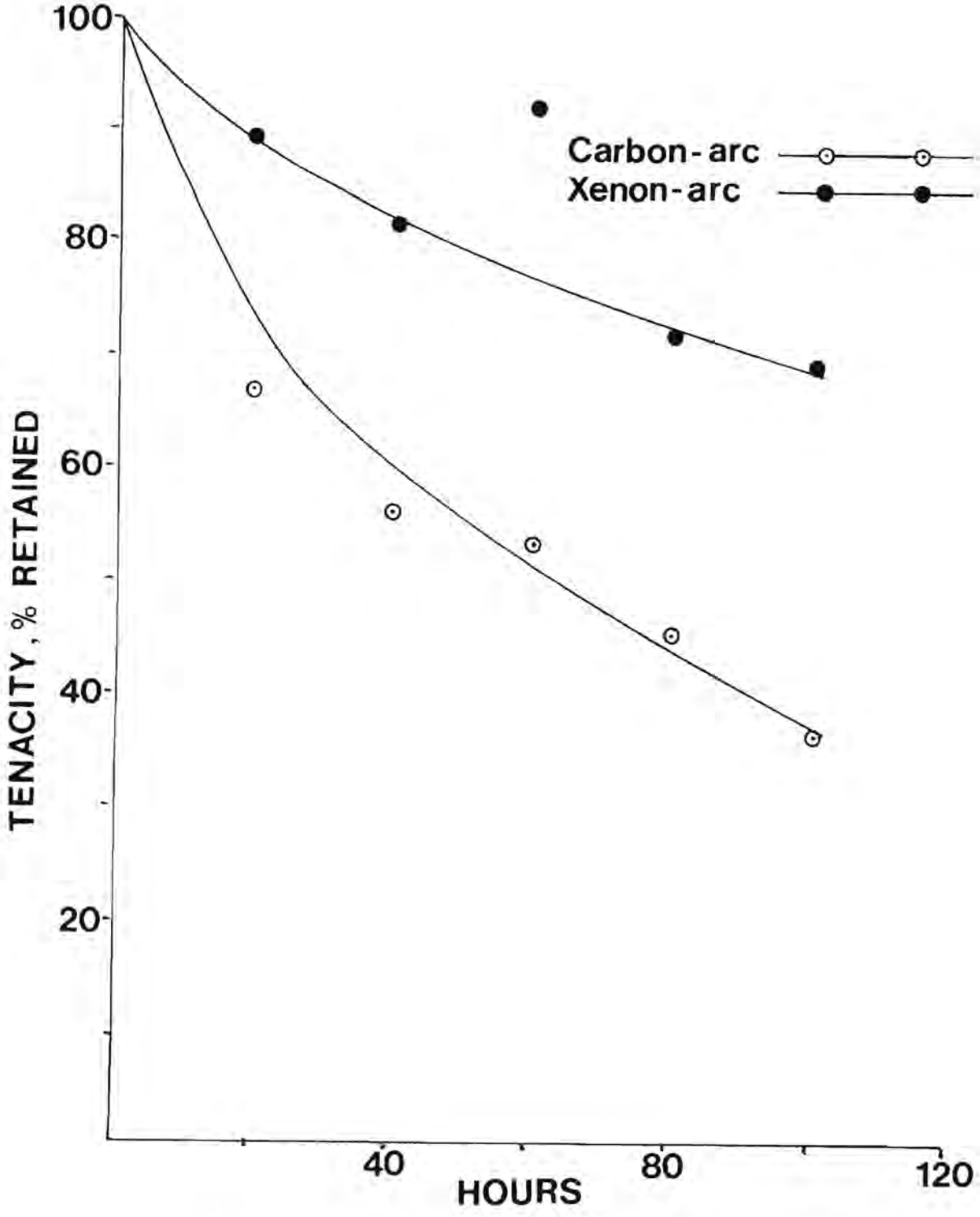

Figure 3. Effect of UV exposure on Nomex yarn tenacity

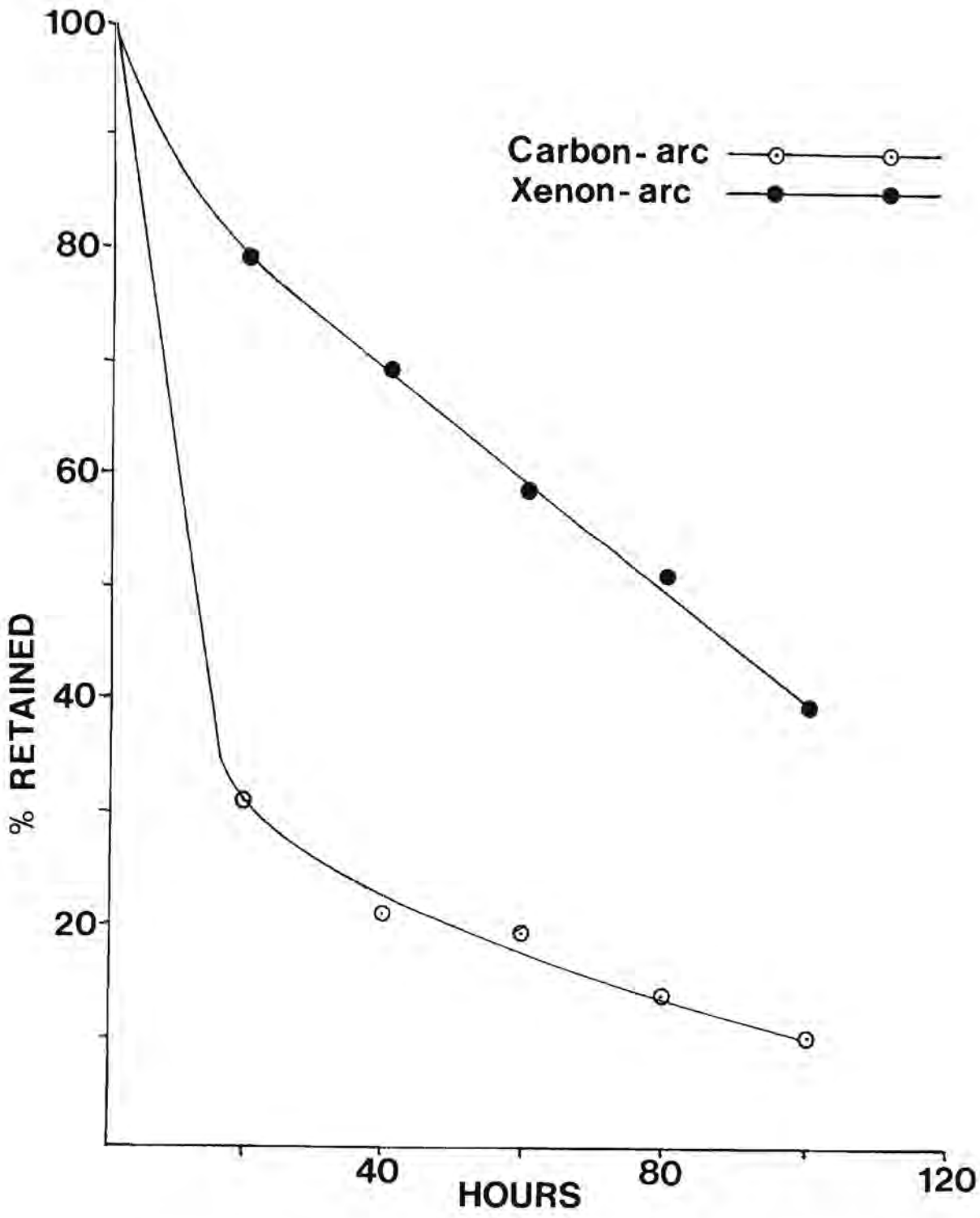

Figure 4. Effect of UV exposure on Nomex yarn elongation

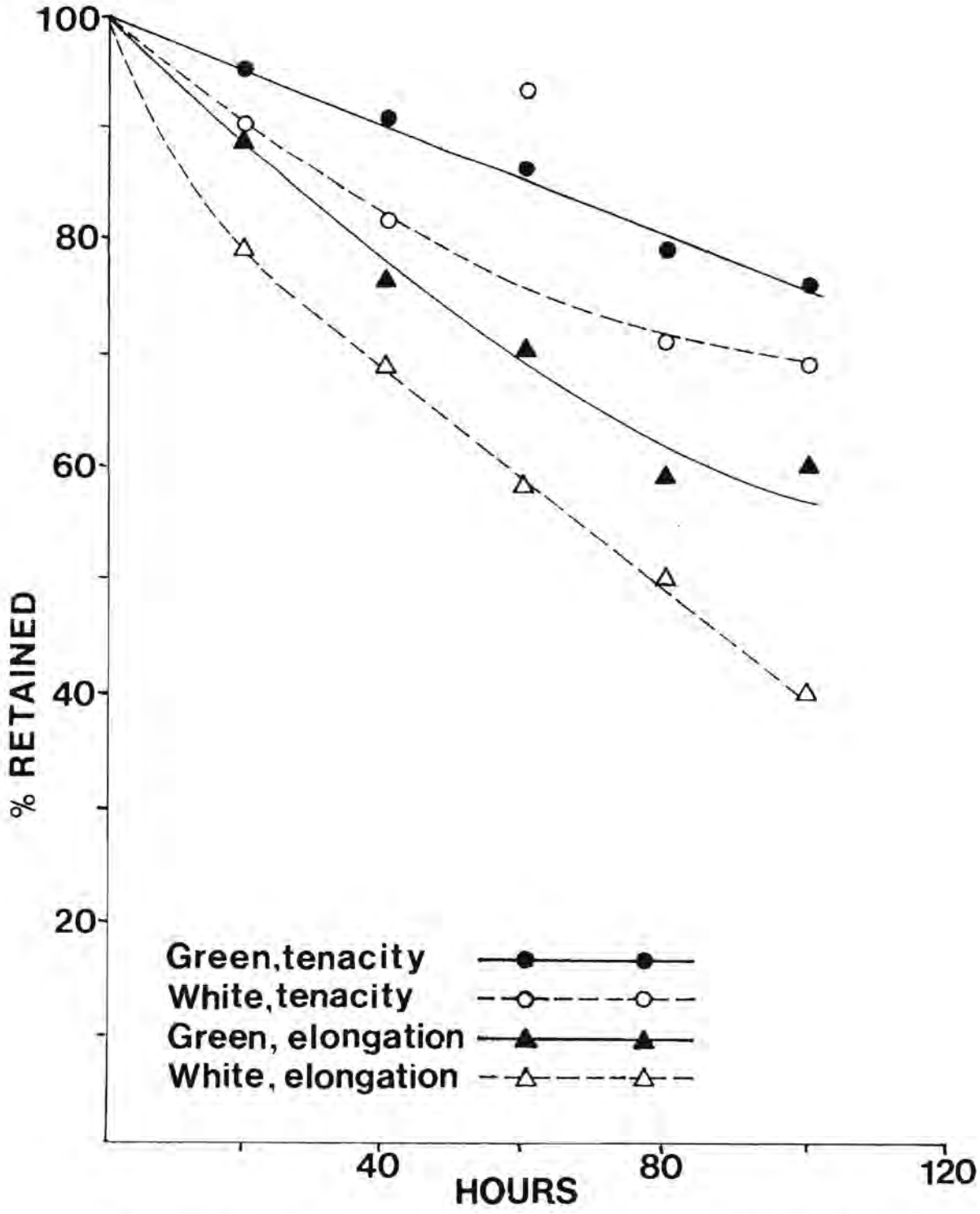

Figure 5. Retention of tenacity and elongation of Nomex Type 430 (white) and Type 433 (sage green) after xenon arc exposure.

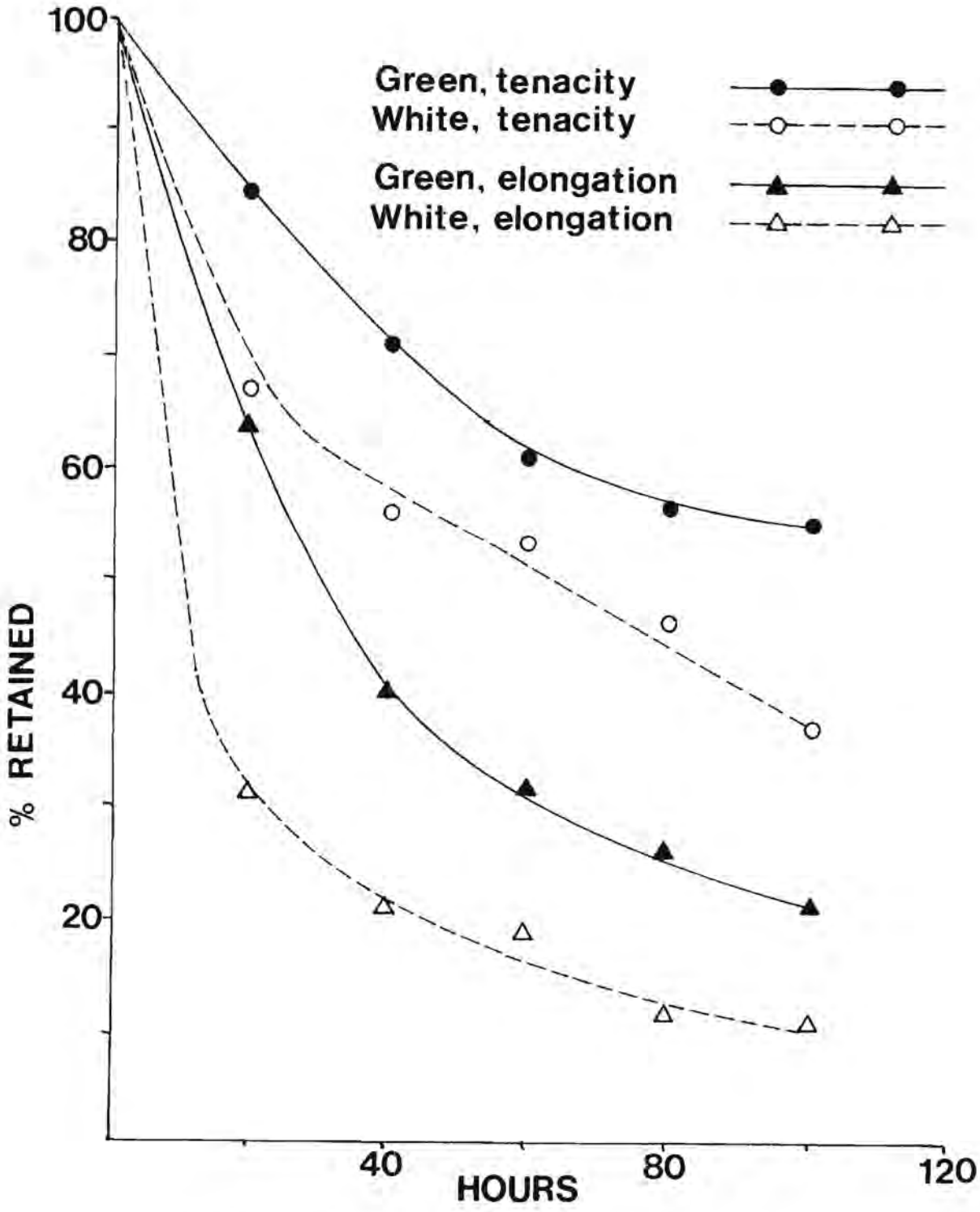

Figure 6. Retention of tenacity and elongation of Nomex Type 430 (white) and Type 433 (sage green) after carbon arc exposure.

It is probable that duPont is adding a UV stabilizer to type 433 Nomex. This stabilizer may be contributing to the improved property retention for this type Nomex. The green pigment in type 433 may also be contributing to the improved UV resistance.

The effect of the treatment process for addition of stabilizer to Nomex type 433 (sage green) yarn samples is shown in Figure 7. Some slight improvement in retention of elongation and in some cases retention of tenacity are observed from the "blank dyeing" alone. This is undoubtedly due to retention of small quantities of residual swelling agent (carrier) in the fiber which acts as a plasticizer in reducing the brittleness resulting from UV degradation. In a few cases, some loss in tenacity is observed for "blank dyed" samples. This probably results from mechanical damage to the yarn during the dyeing operations. The changes observed due to the treatment process were small enough not to adversely affect the conclusions derived from the stabilizer screening studies. All subsequent screening studies on the effects of stabilizers on UV stability of Nomex were conducted on Nomex type 433 (sage green) yarn. The carbon-arc Fade-Ometer was the principal exposure source used since it gives more rapid degradation and was likely, therefore, to more clearly identify useful stabilizers. Xenon arc exposures were carried out on samples containing a number of potential stabilizers for comparison with the carbon-arc data.

2. Exposure Studies on Nomex Treated with UV Absorbers

Retention of tenacity and elongation of Nomex samples containing UV absorbers compared to control samples after exposure for 20,40,60,80, and 100 hours in the carbon arc Fade-Ometer are shown in Figures 8 - 17. Similar results for xenon arc exposures are shown in Figures 18 - 23.

Nomex yarn containing Leucophor EFR showed a significant reduction in both tenacity and elongation in all exposure experiments (Figures 8 and 18). This material is clearly capable of phototendering Nomex. Samples containing Uvitex WGS (Figures 9 and 19) indicate that this optical brightener has little or no effect on property retention on UV exposure. A similar conclusion is indicated by results on samples containing Uvitex RBNAD (Figure 10 and 20). Results are less clear for Uvitex NFW containing samples (Figure 11 and 21). This bright-

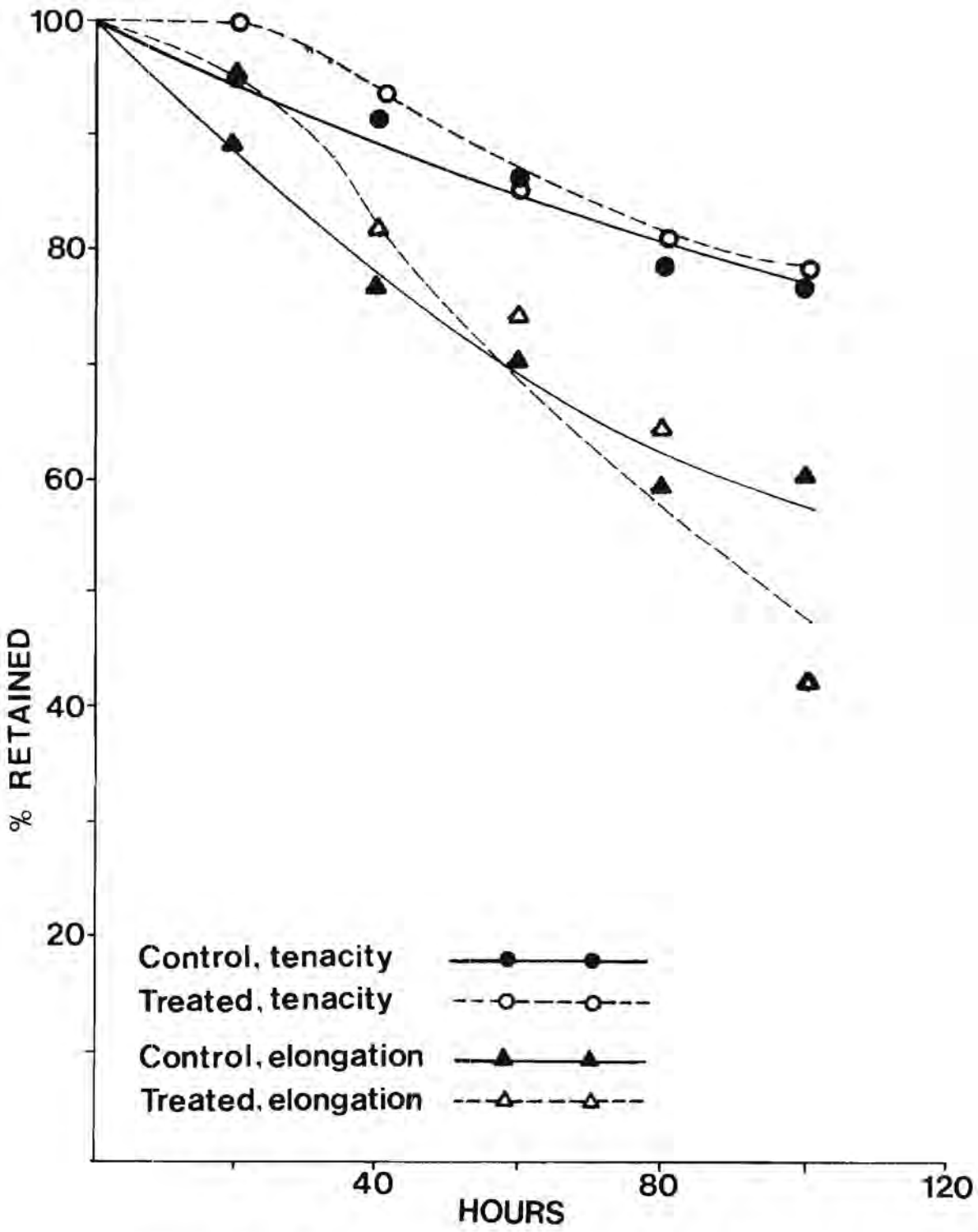

Figure 7. Retention of tenacity and elongation of Nomex Type 433 control and blank dyed after xenon arc exposure.

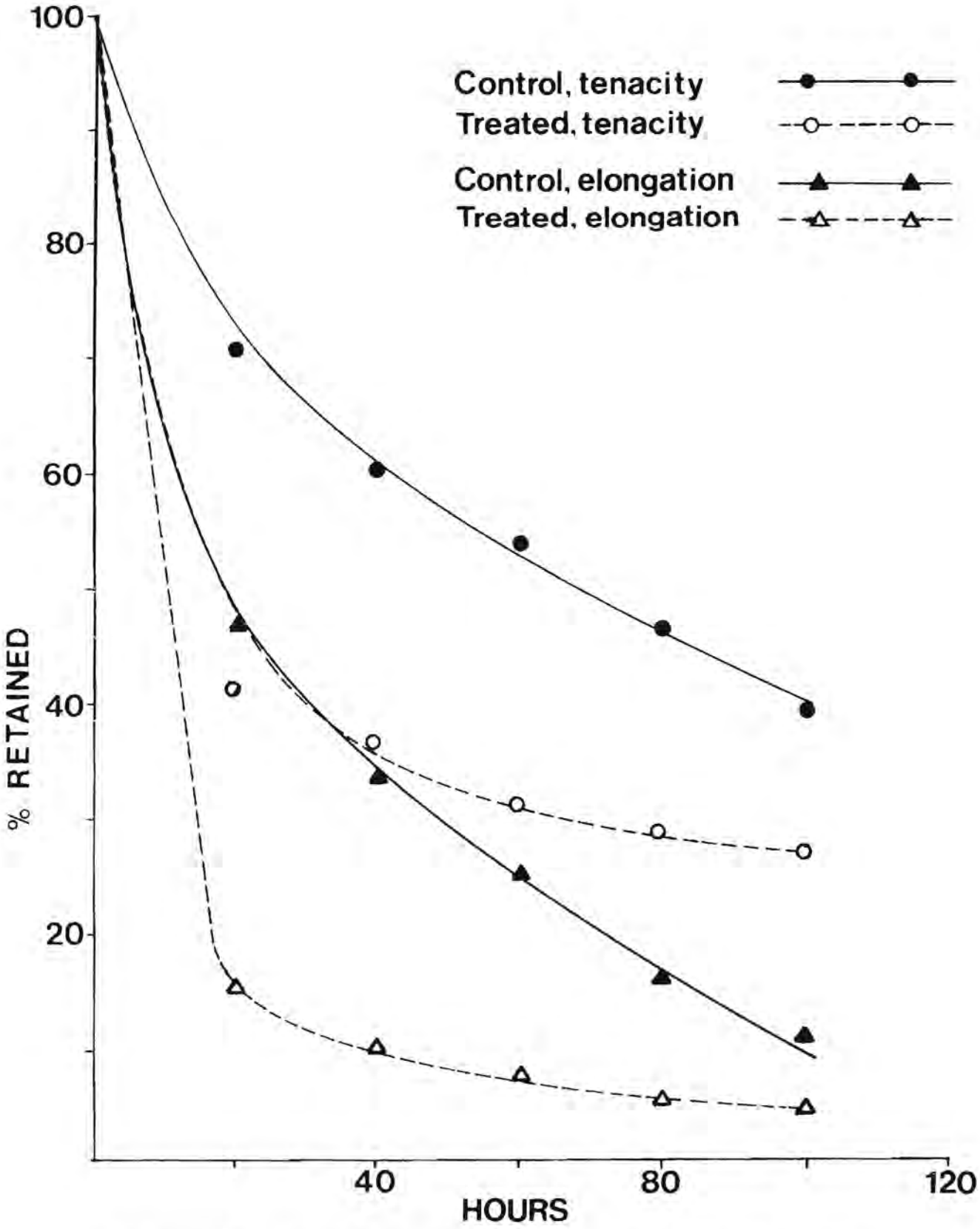

Figure 8 - Retention of tenacity and elongation of Nomex Type 433 containing Leucophor EFR compared to control after carbon arc exposure.

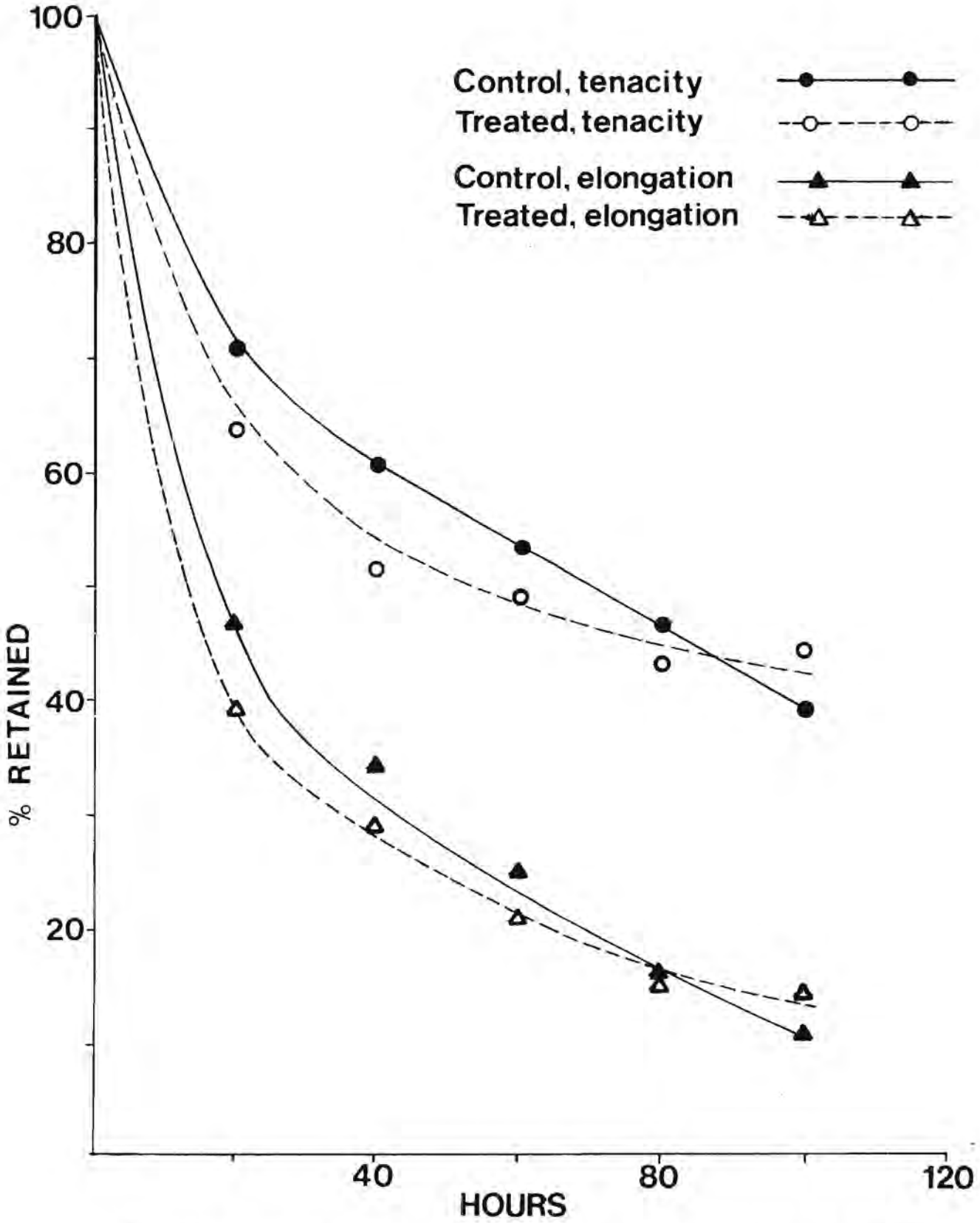

Figure 9. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex WGS compared to control after carbon arc exposure.

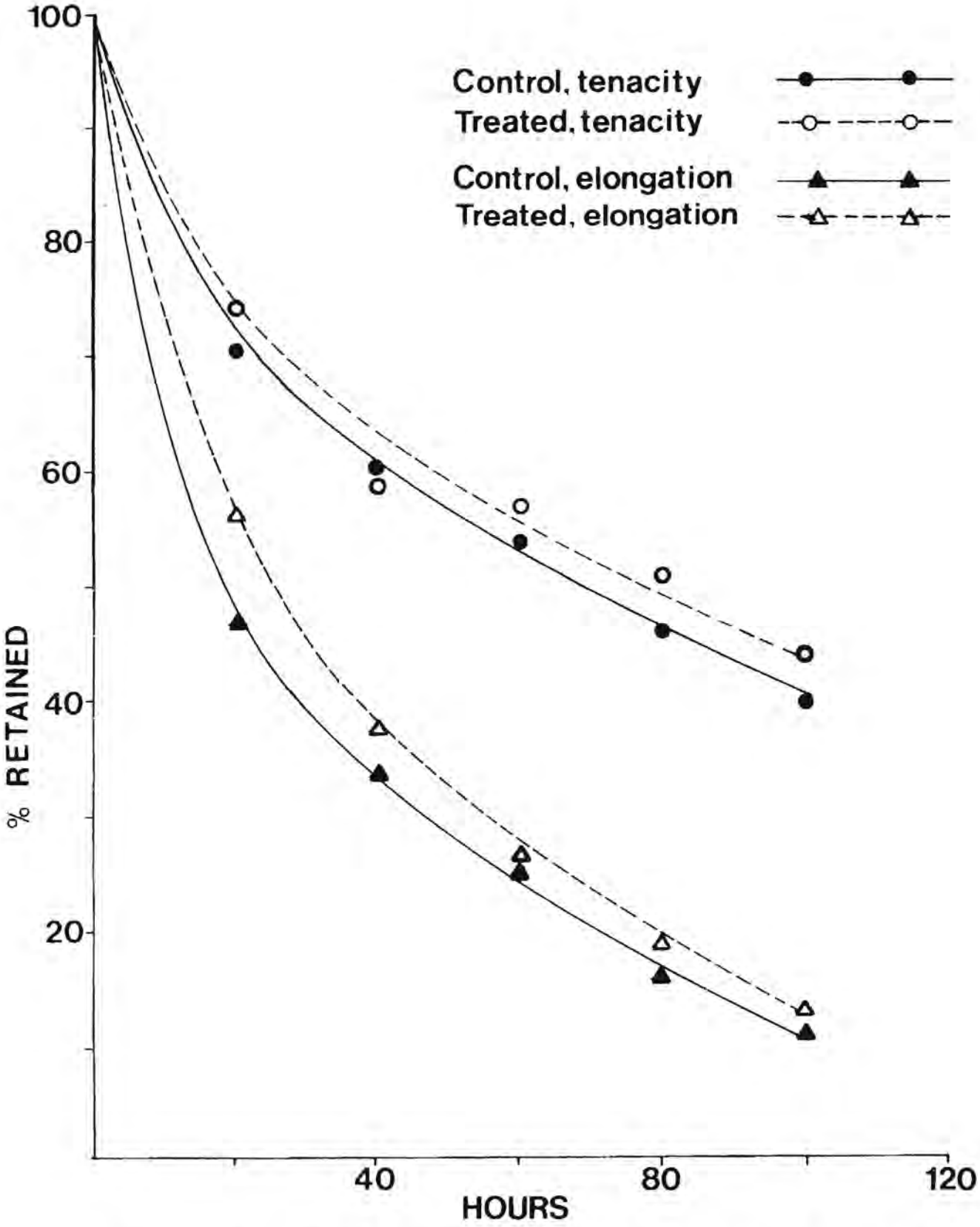

Figure 10. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex RBNAD compared to control after carbon arc exposure.

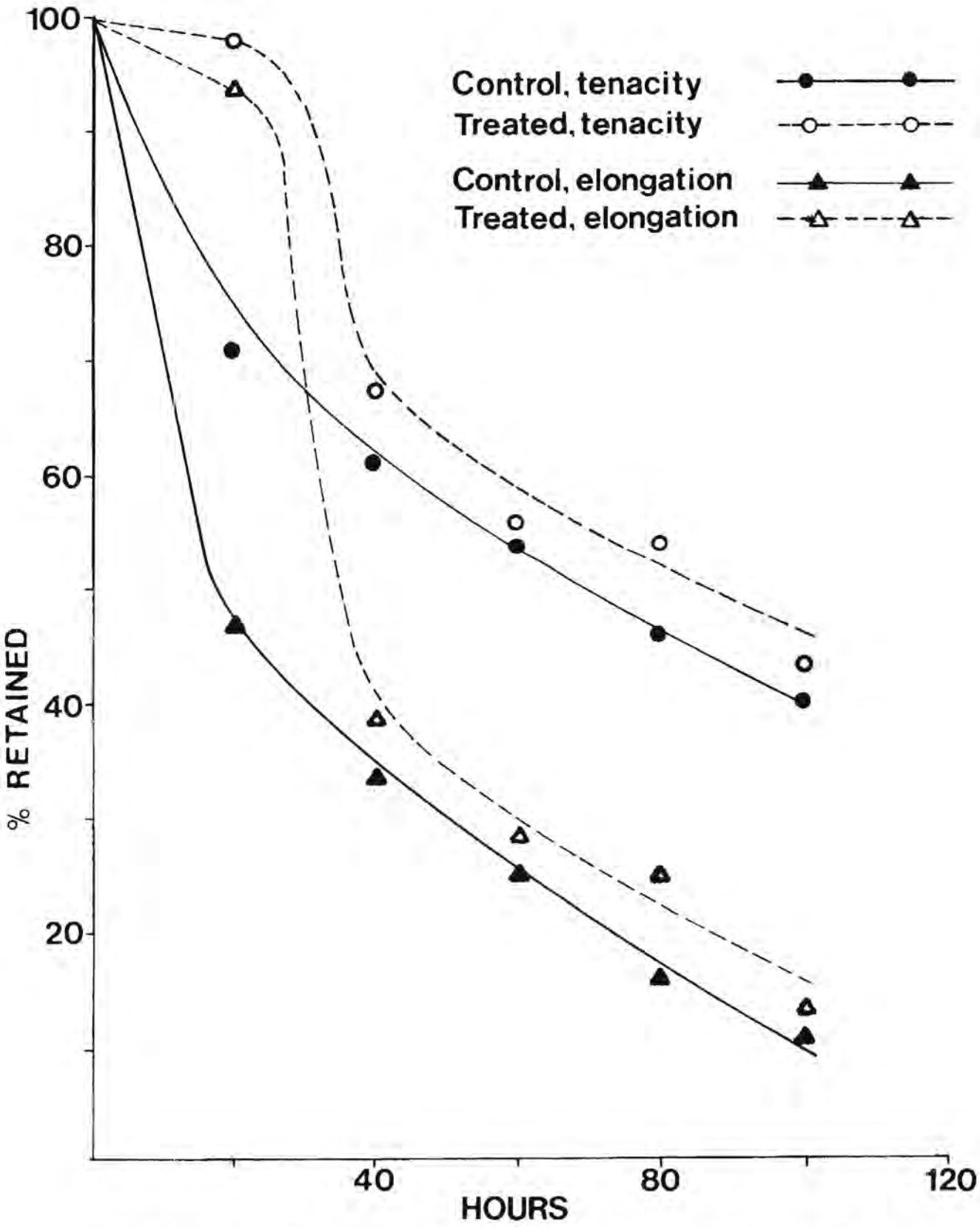

Figure 11. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex NFW compared to control after carbon arc exposure.

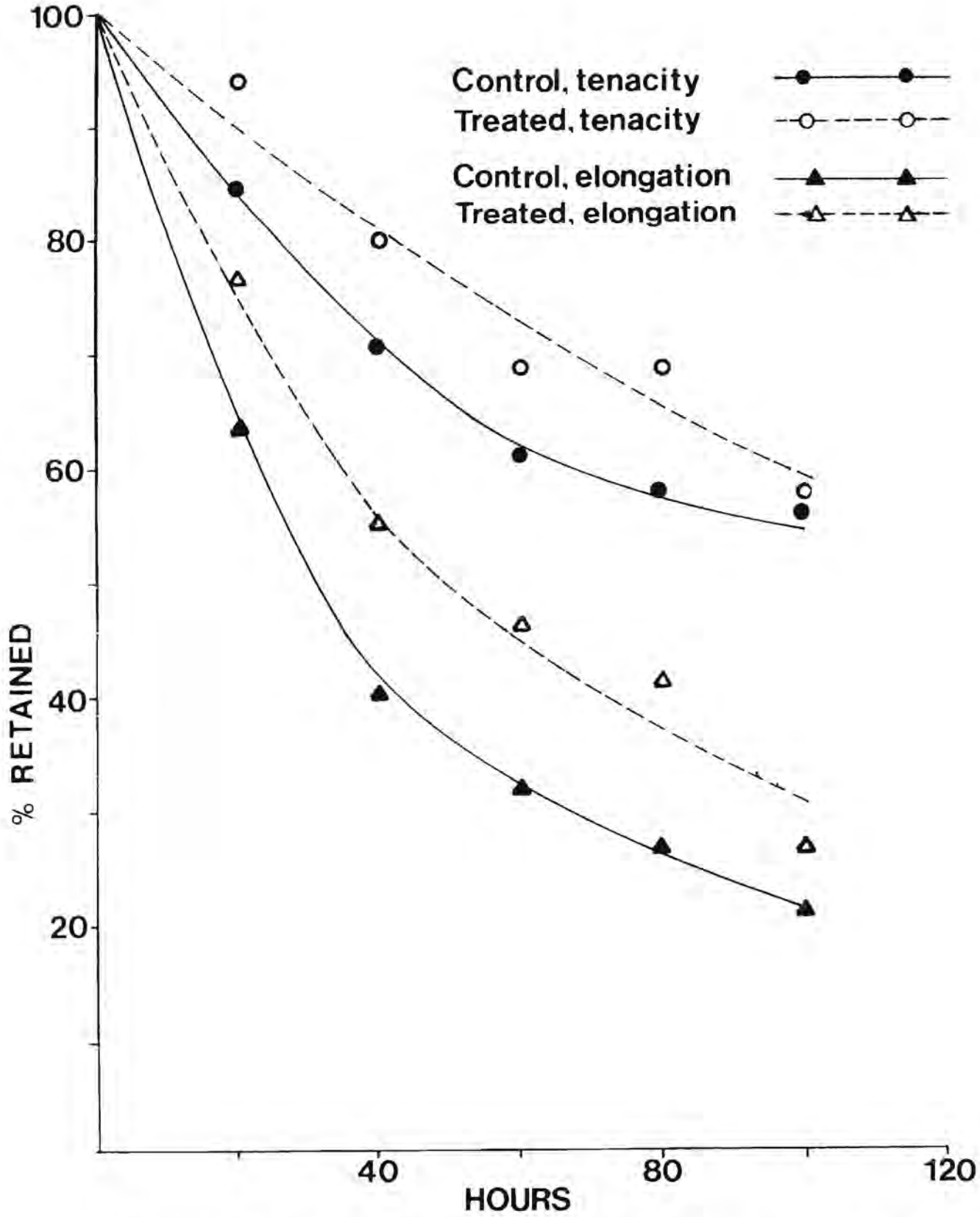

Figure 12. Retention of tenacity and elongation of Nomex Type 433 containing Blancophor AW compared to control sample after carbon arc exposure.

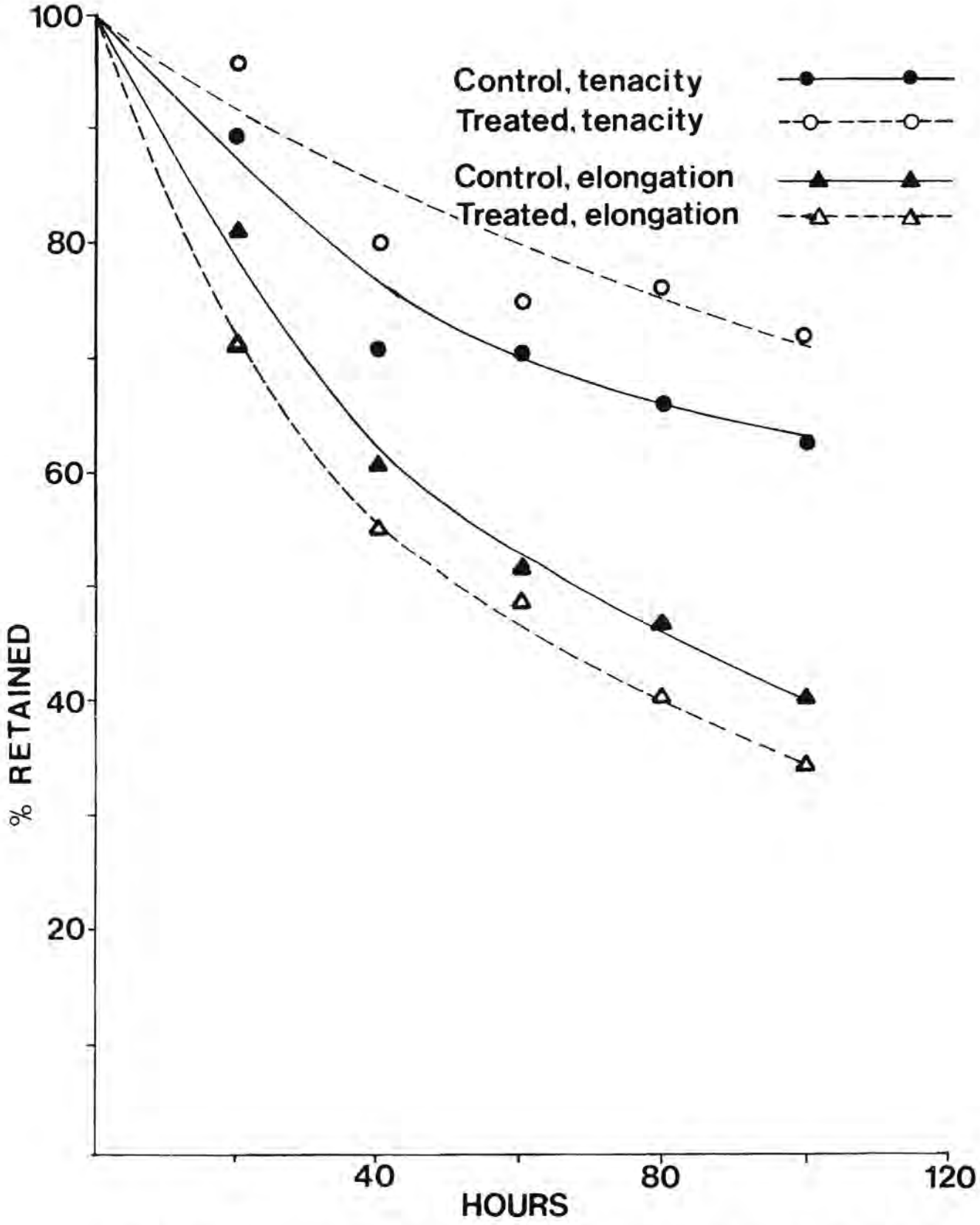

Figure 13. Retention of tenacity and elongation of Nomex Type 433 containing Tinuvin P compared to control after carbon arc exposure.

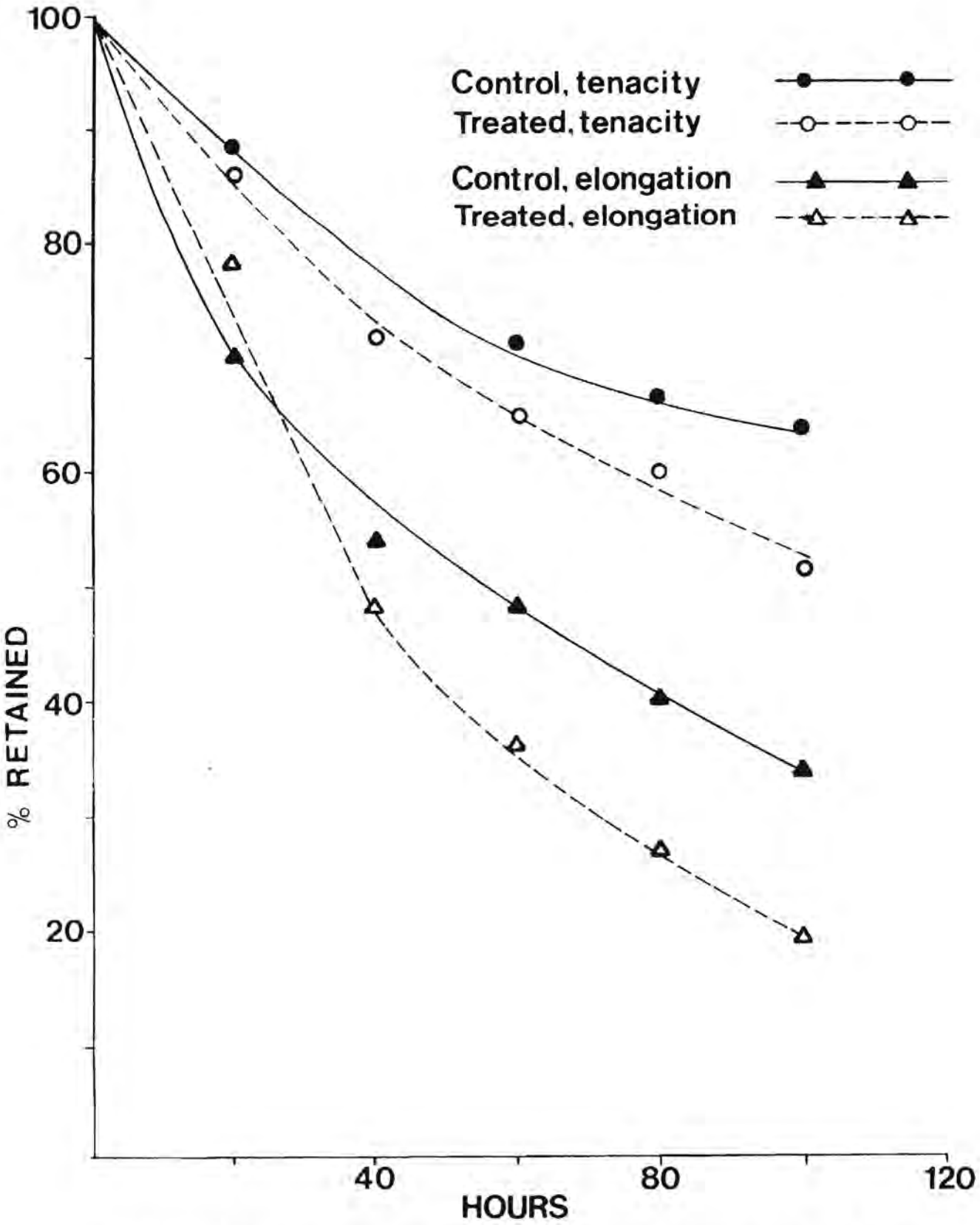

Figure 14. Retention of tenacity and elongation of Nomex Type 433 containing Tinuvin 327 compared to control after carbon arc exposure.

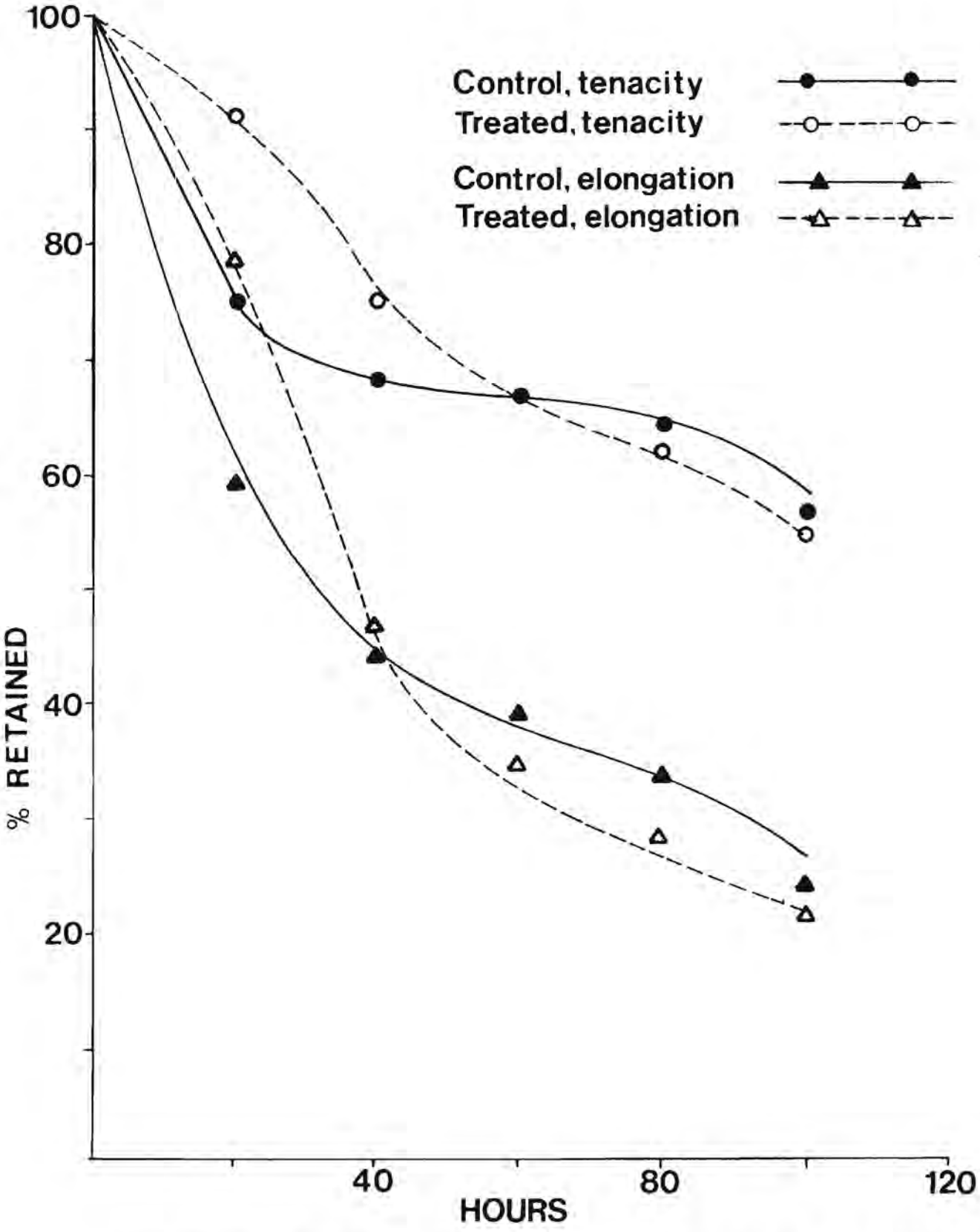

Figure 15. Retention of tenacity and elongation of Nomex Type 433 containing Cyasorb UV-800 compared to control after carbon arc exposure.

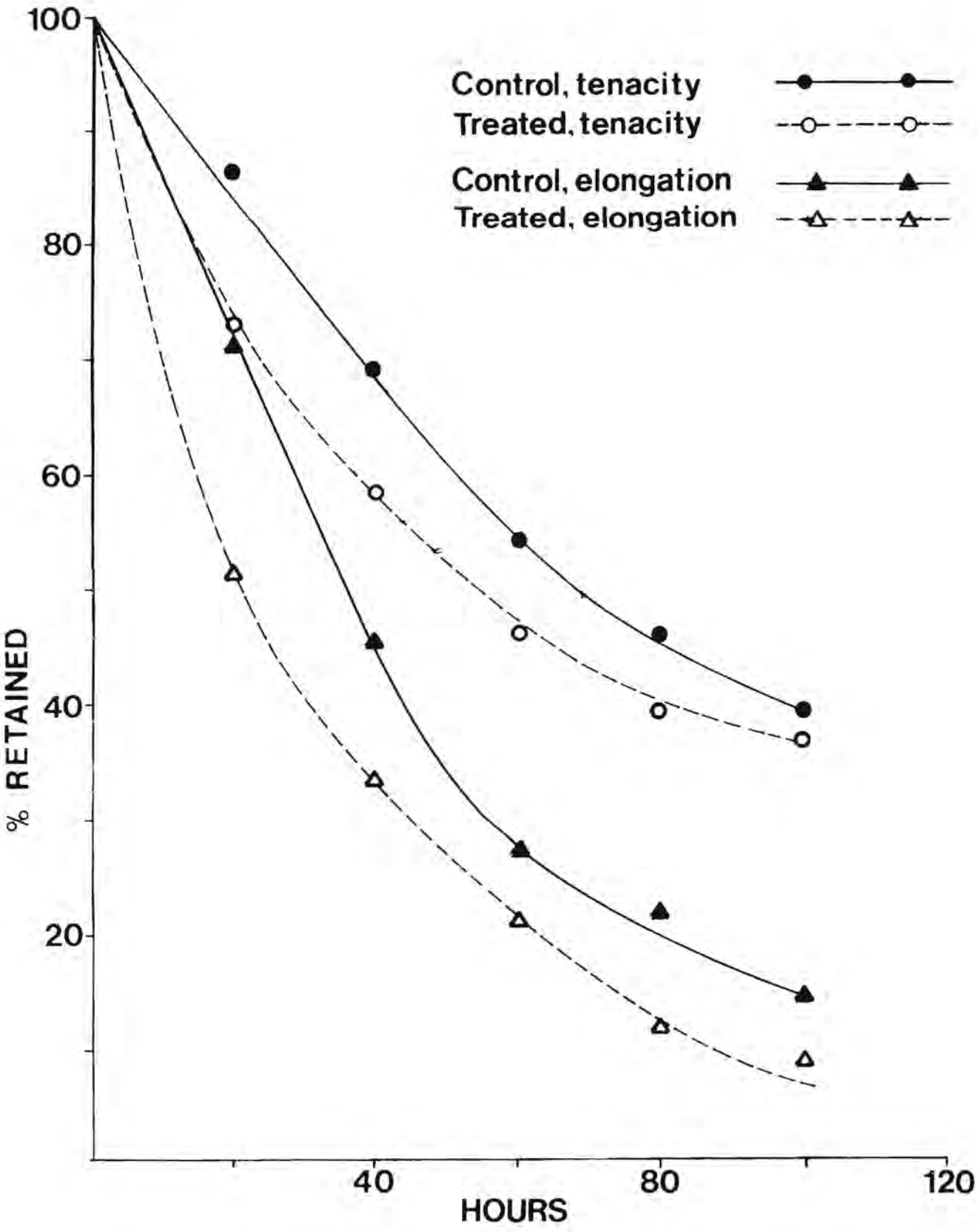

Figure 16. Retention of tenacity and elongation of Nomex Type 433 containing Tinuvin 770 compared to control after carbon arc exposure.

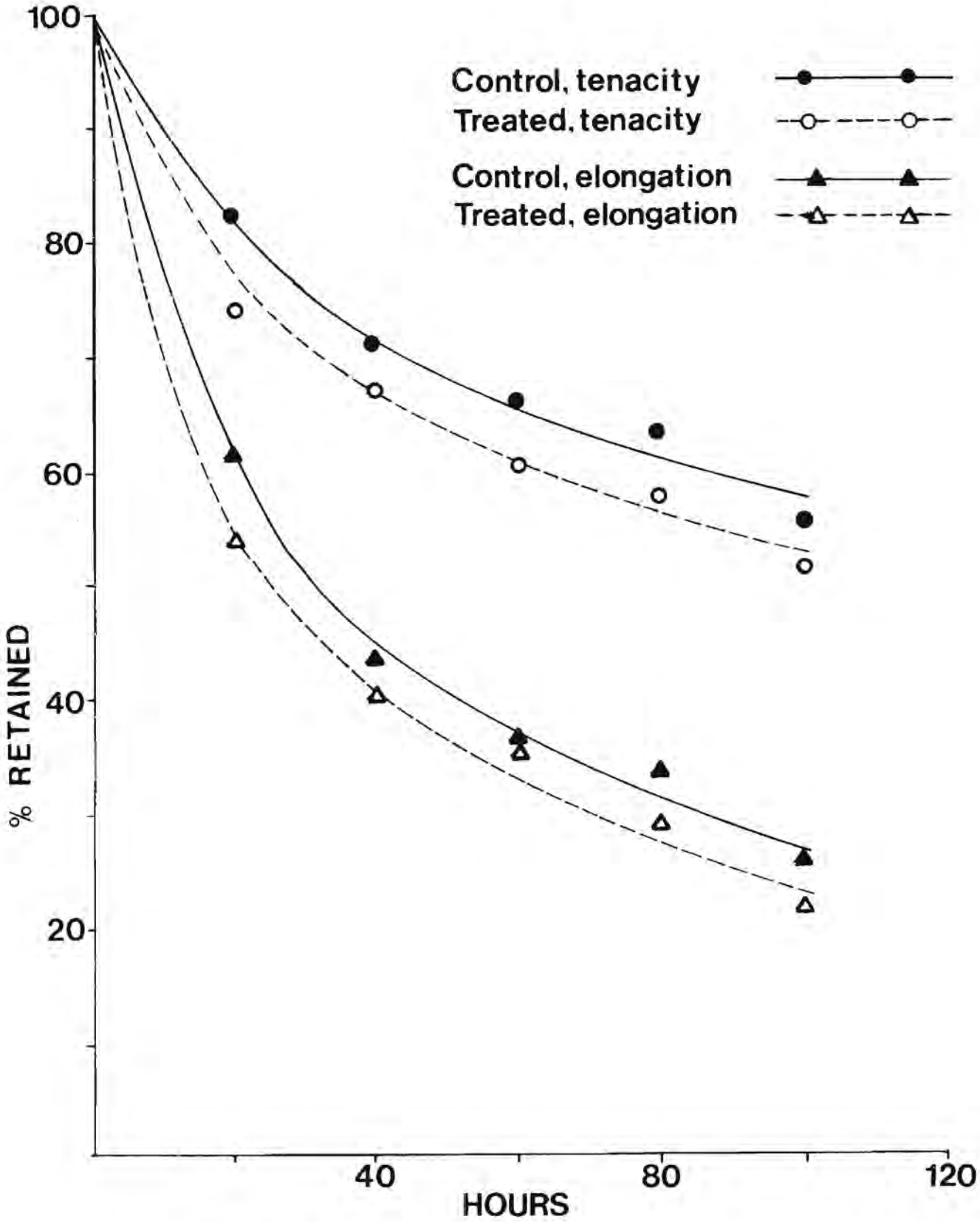

Figure 17. Retention of tenacity and elongation of Nomex Type 433 containing Eastman Inhibitor RMB compared to control after carbon arc exposure.

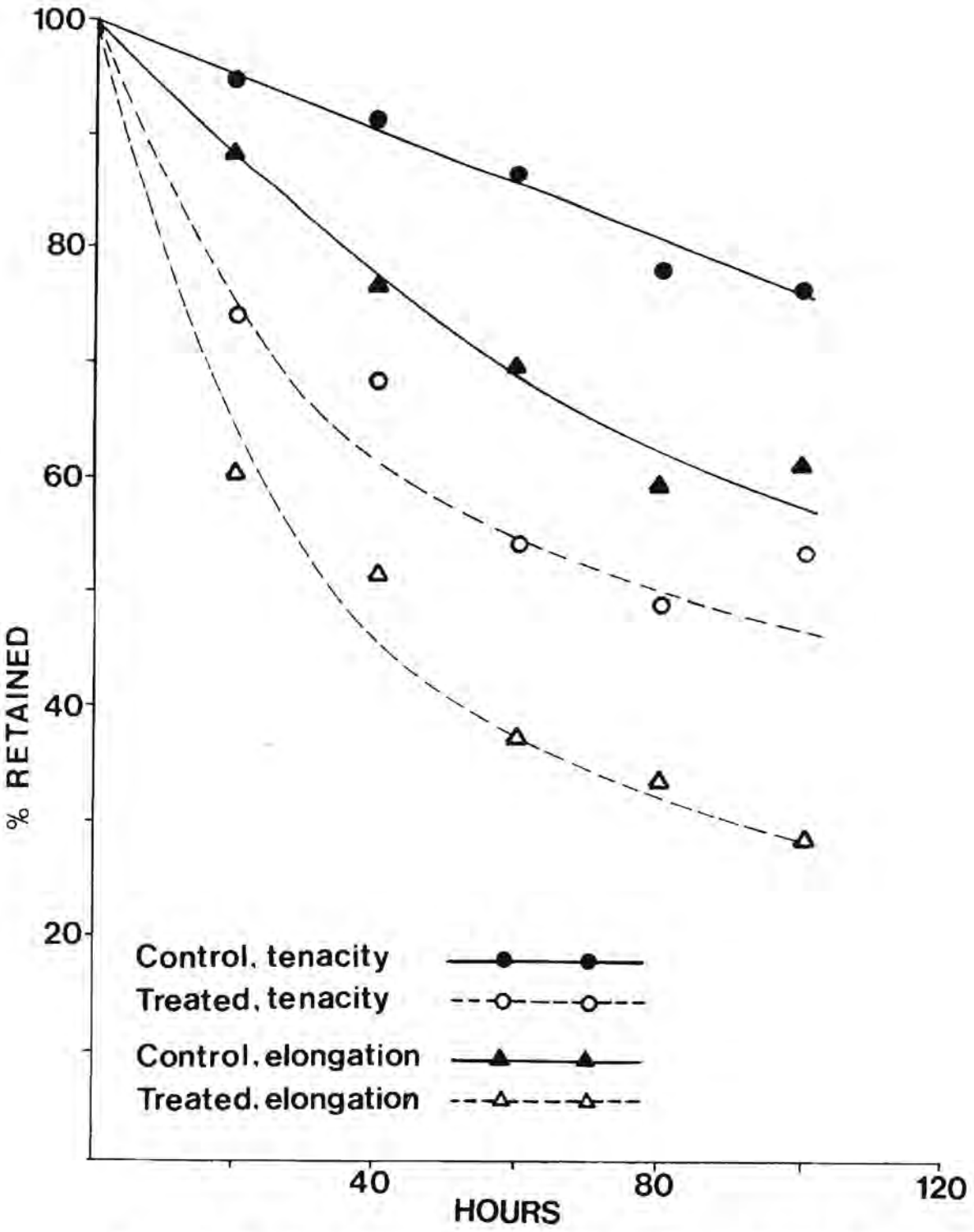

Figure 18. Retention of tenacity and elongation of Nomex Type 433 containing Leucophor EFR compared to control sample after xenon arc exposure.

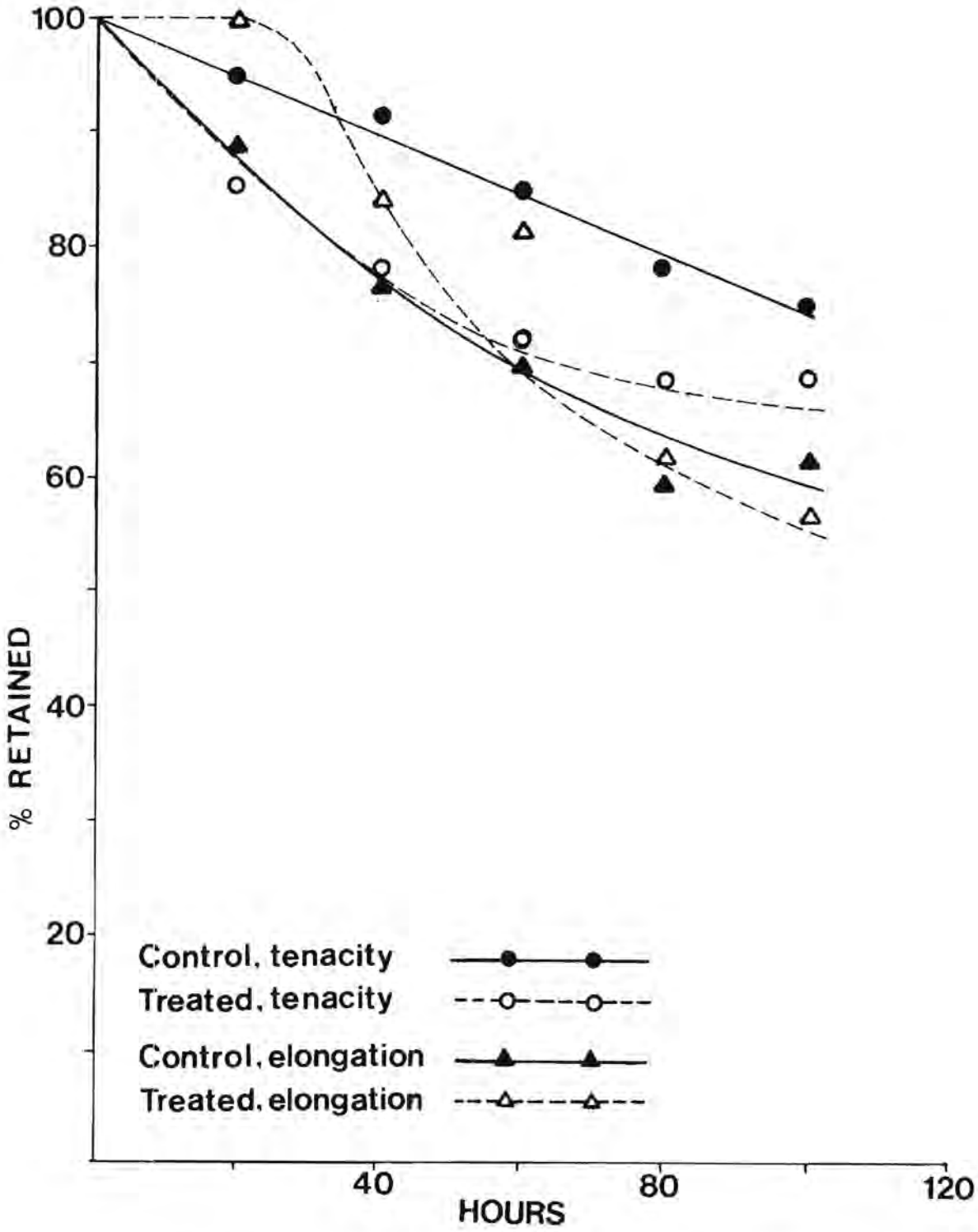

Figure 19. Retention of tenacity and elongation of Nomex Type 433 xenon containing Uvitex WGS compared to control sample after xenon arc exposure.

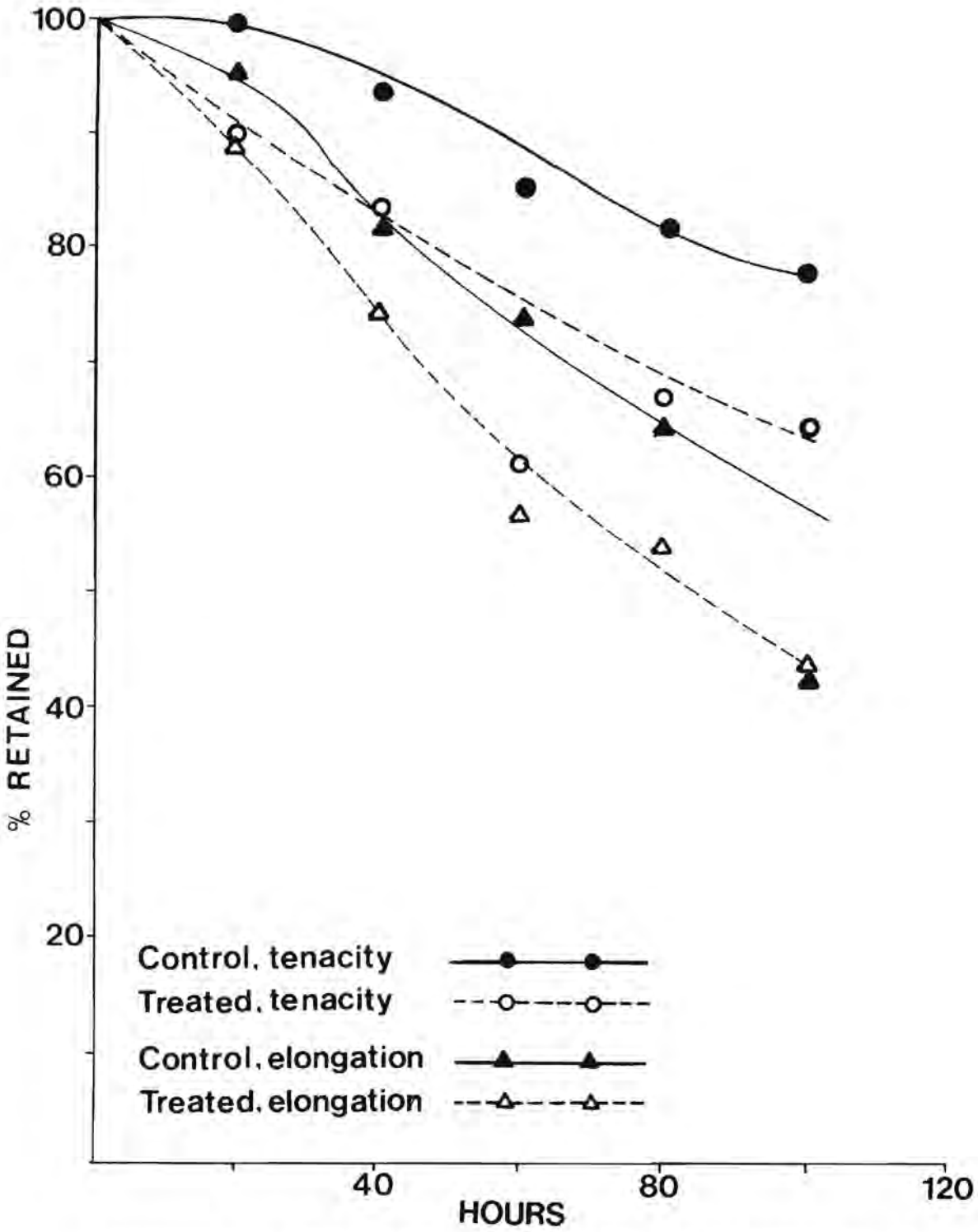

Figure 20. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex RBNAD compared to control after xenon arc exposure.

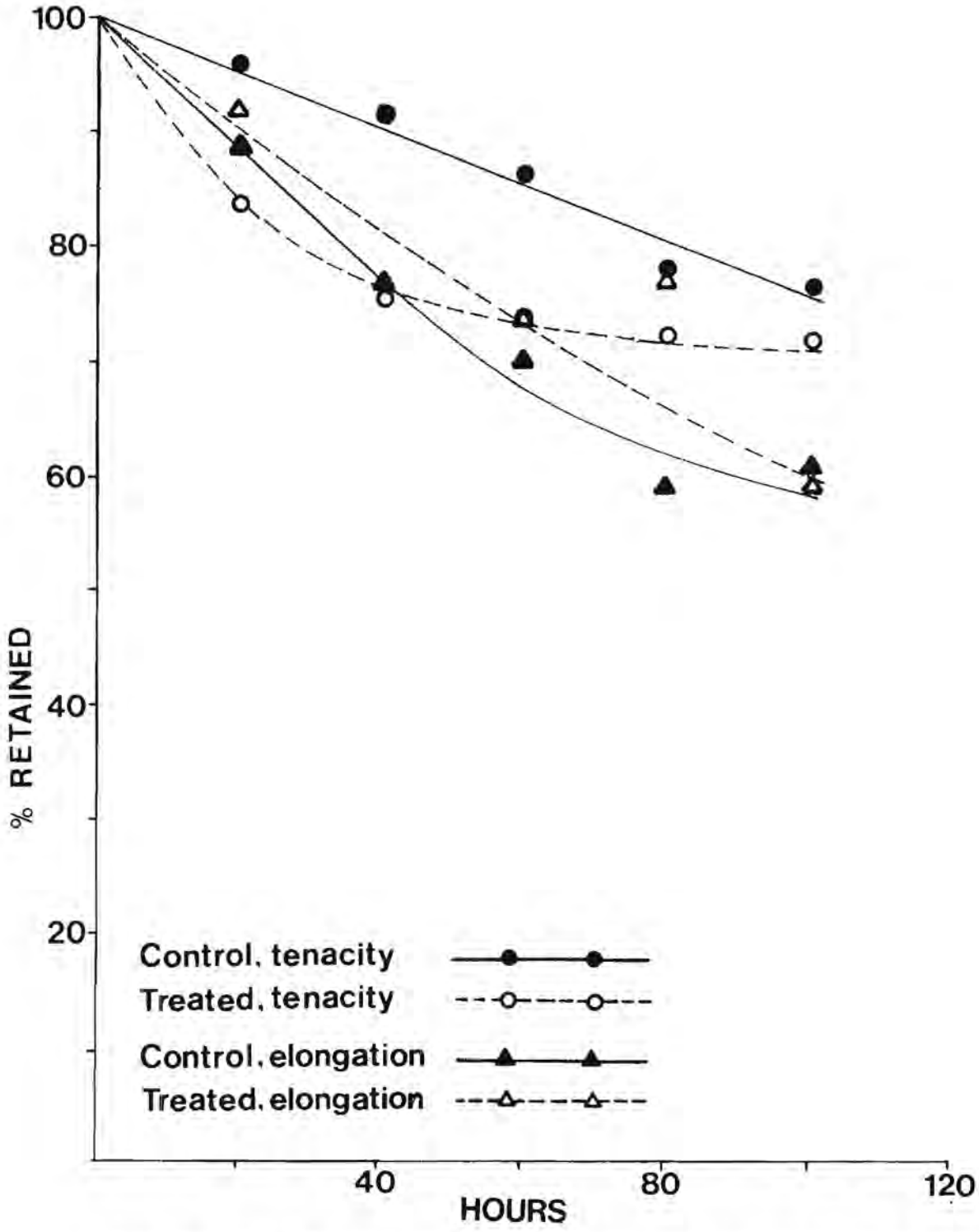

Figure 21. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex NFW compared to control sample after xenon arc exposure.

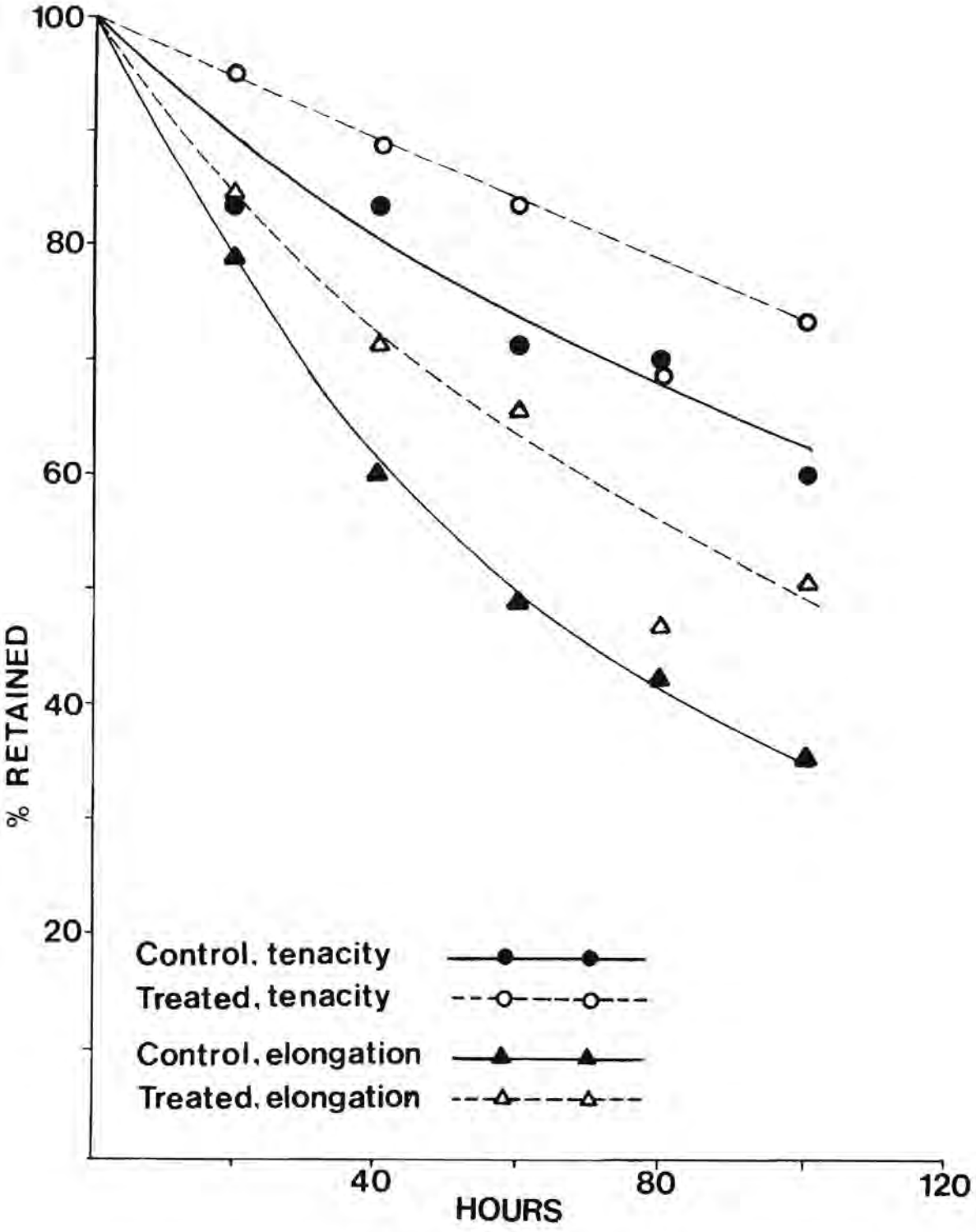

Figure 22. Retention of tenacity and elongation of Nomex Type 433 containing Blancophor AW compared to control sample after xenon arc exposure.

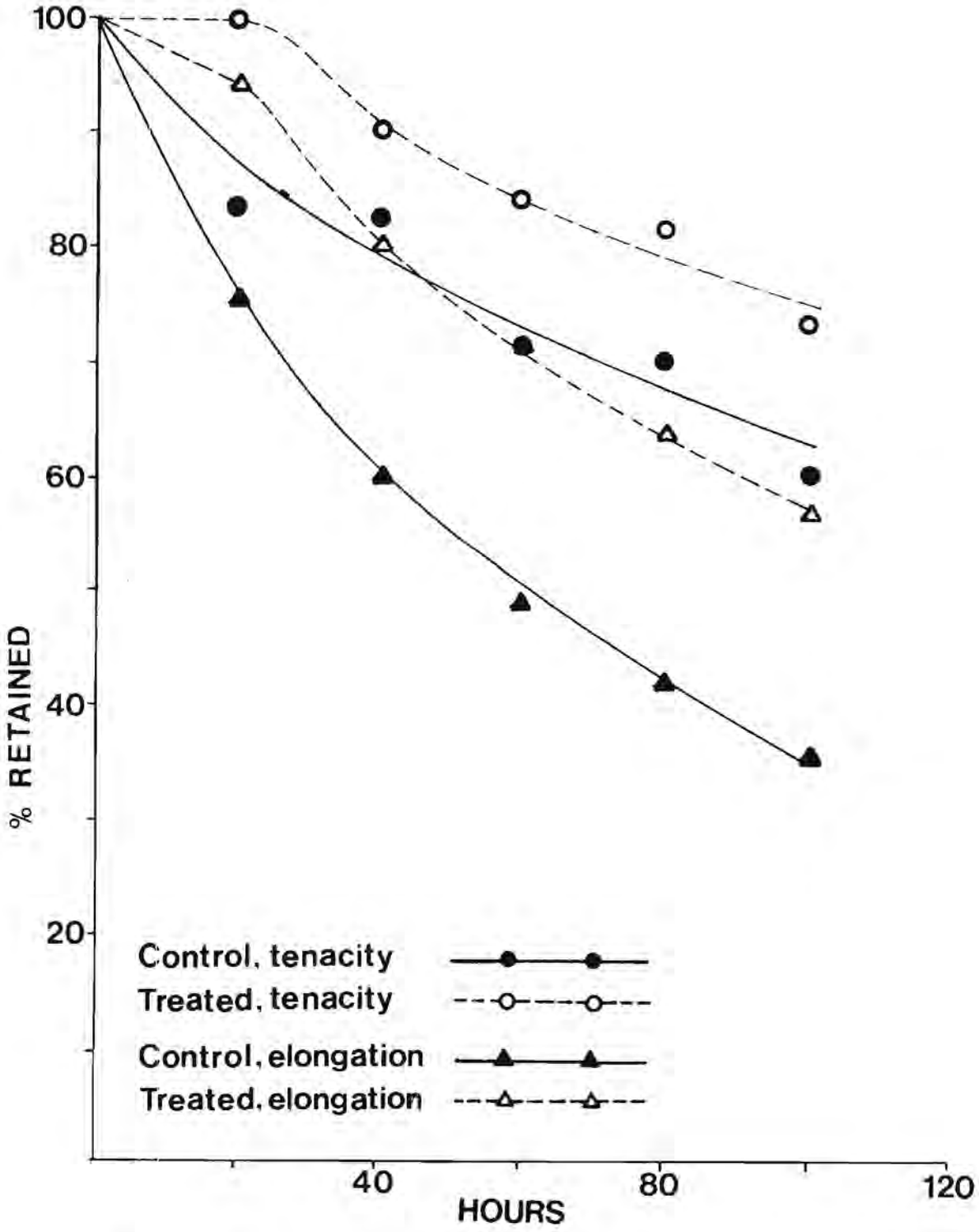

Figure 23. Retention of tenacity and elongation of Nomex Type 433 containing Tinuvin P compared to control after xenon arc exposure.

ener appears to have some protective effect in the first 20 hours of carbon-arc exposure. The stabilizing effect is rapidly lost however, probably due to degradation of the optical brightener itself. A similar stabilization is not observed for xenon arc exposure. The higher output of the xenon arc in the UV region may give a more rapid degradation of the Uvitex NFW. It should be noted that results for xenon exposure of the Uvitex NFW containing sample appear to be somewhat erratic. It does, however, apparently provide some small stabilizing effect on Nomex degradation.

The most promising of the optical brighteners for Nomex stabilization appears to be Blancophor AW (Figures 12 and 22). This material gave a clear stabilizing effect at all exposure times. A statistical analysis of the data confirmed that Blancophor AW containing Nomex has significantly greater retention of tenacity and elongation than the blank dyed sample.

Results for samples containing standard UV absorbers indicate that of the absorbers tested only Tinuvin P gave long term improvement in retention of tensile strength and elongation. Cyasorb UV-800 was effective during the first 40 hours of exposure (Figure 15) but gave tensile strength retention no better than the control after 100 hours. Degradation of the absorber itself may be responsible for this result. Tinuvin 327 (Figure 14) and Tinuvin 770 (Figure 16) both appear to reduce the stability of Nomex. This result was surprising in view of the beneficial effect exhibited by Tinuvin P. One other UV screening agent of a different chemical structure than the benzotriazoles was also studied. Eastman Inhibitor RMB (Resorcinol Monobenzoate) which rearranges to give 2,4 - dihydroxybenzophenone was added to Nomex and the samples exposed to the carbon arc Fade-Ometer. Results are shown in Figure 17. These results suggest that benzophenone type stabilizers do not appear to be effective on Nomex.

The retention of tenacity and elongation of Nomex samples containing Tinuvin P is shown in Figures 13 and 23. These data clearly indicate that a stabilizing effect is observed at all exposure times.

This study of UV screening agents for stabilization of Nomex suggests that some optical brighteners and UV absorbers can have a beneficial effect on Nomex degradation. In both cases the effect is small. Both Blan-

cophor AW and Tinuvin P were selected for further study is subsequent phases of the project.

3. Exposure Studies on Nomex Treated With Antioxidants

The antioxidants investigated in this study are listed in Table 1. These materials were added to Nomex yarn Type 433 by the dyeing procedures described previously. The antioxidants selected are of the hindered phenol type with other structural features designed to inhance the antioxidant characteristics.

Samples of yarn containing the antioxidants were exposed to the carbon arc Fade-Ometer for periods up to 100 hours. Tenacity and elongation of the yarn samples were determined before and after exposure.

The percent retention of tenacity and elongation for samples containing Irganox 1035 is shown in Figure 24. This antioxidant gives no perceptible difference in the stability of Nomex.

Similar results for samples containing Plastanox 1735, Irganox 1010, Irganox 1098 and CSA-316 are shown in Figures 25,26 and 27, and 28. All of these antioxidants reduce the stability of Nomex slightly. The reasons for this effect are not known at the present time.

The results of these studies suggest that antioxidants as a class show little promise as stabilizers for Nomex. Since these materials are primarily effective in free radical oxidative degradation reactions, the results at least indicate that such reaction mechanisms are not involved in Nomex UV degradation.

4. Exposure Studies on Nomex Treated With Quenchers

Six compounds reported to stabilize polymeric systems by a quenching mechanism have been added to Nomex. The compounds investigated are given in Table 1. All were added to Nomex type 433 yarn by the modified dyeing procedure described previously.

Samples containing quenchers were exposed in the carbon arc Fade-Ometer for up to 100 hours and exposed and control (blank dyed) samples tested on the Instron.

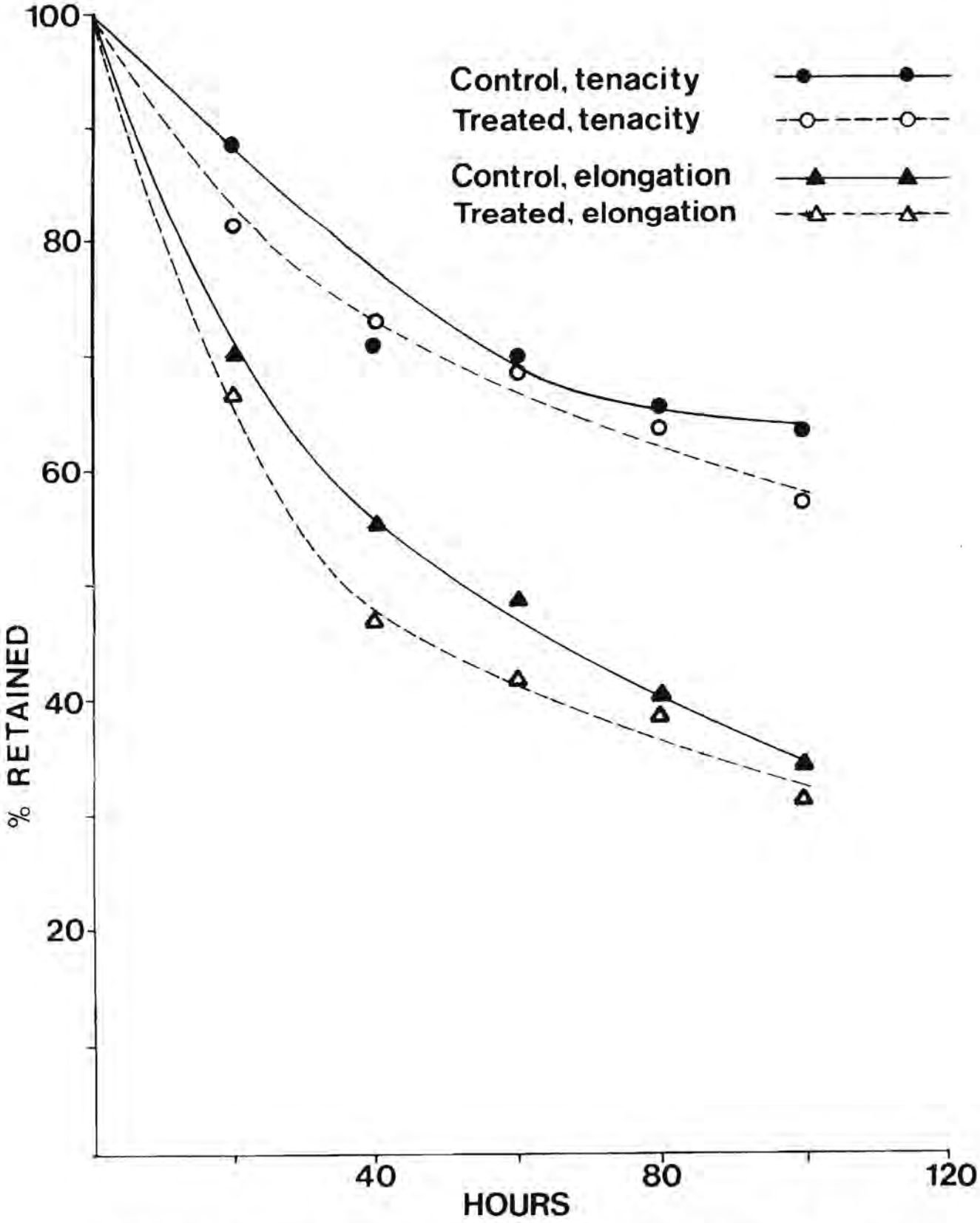

Figure 24. Retention of tenacity and elongation of Nomex Type 433 containing Irganox 1035 compared to control sample after carbon arc exposure.

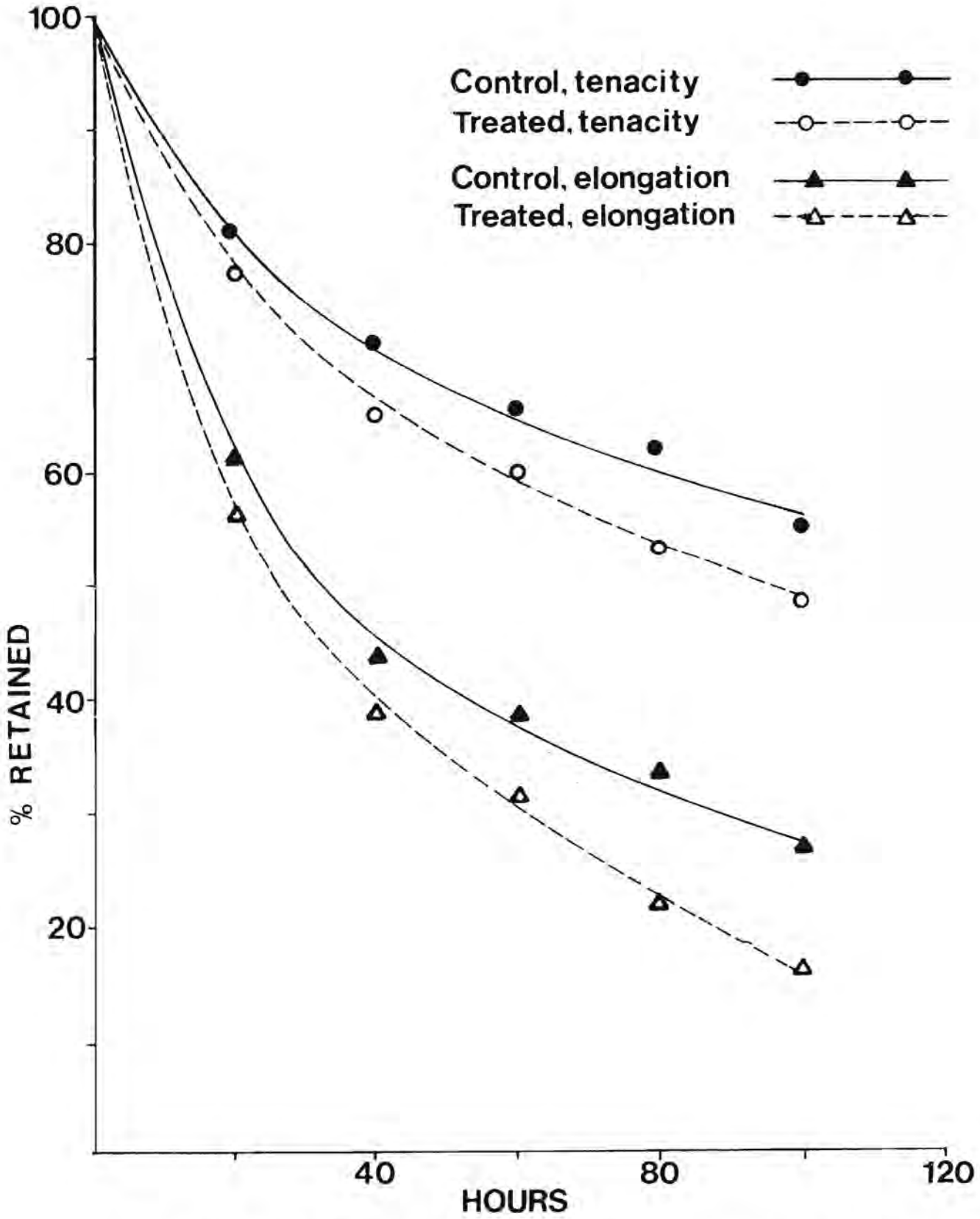

Figure 25. Retention of tenacity and elongation of Nomex Type 433 containing Plastanox 1735 compared to control sample after carbon arc exposure.

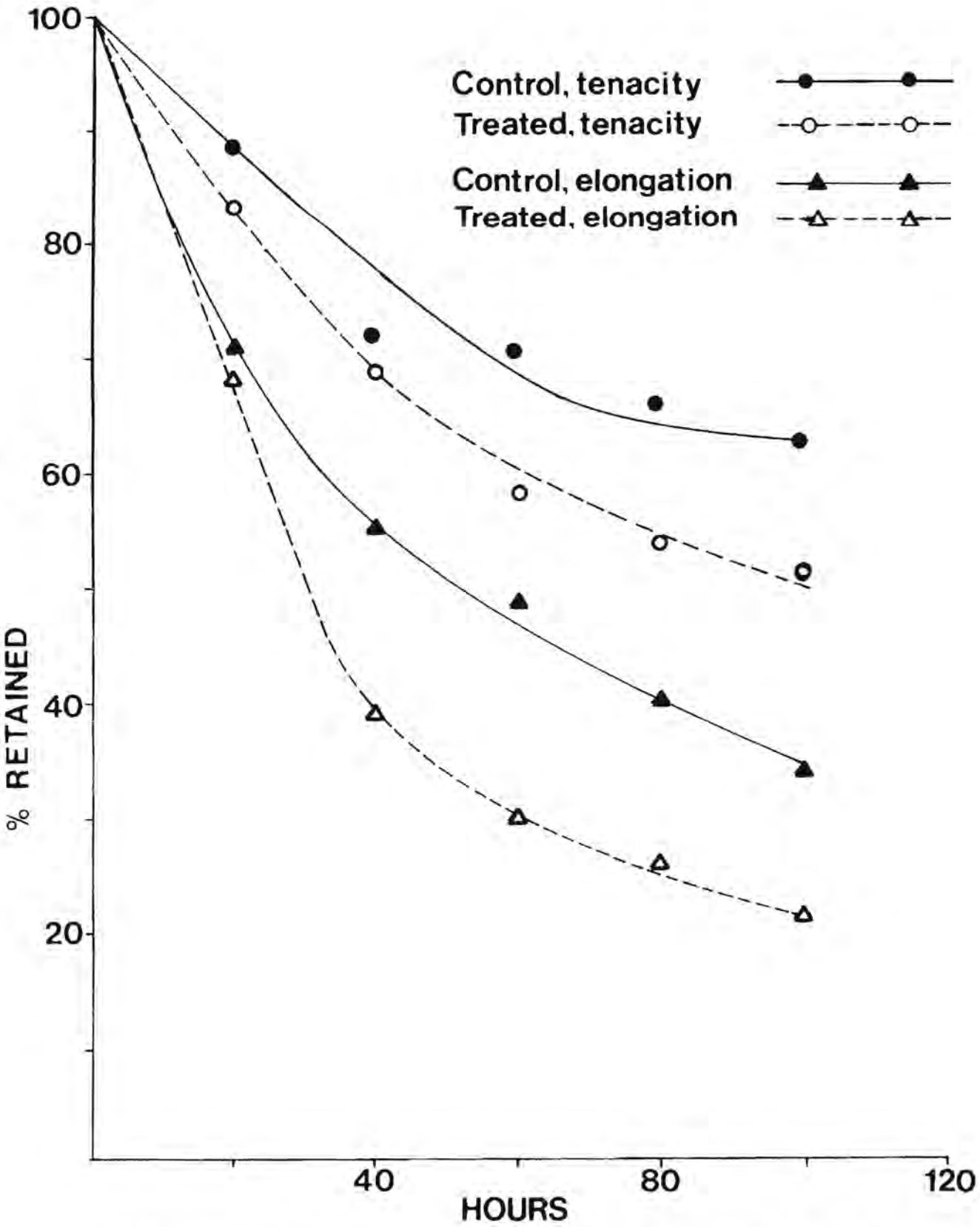

Figure 26. Retention of tenacity and elongation of Nomex Type 433 containing Irganox 1010 compared to control sample after carbon arc exposure.

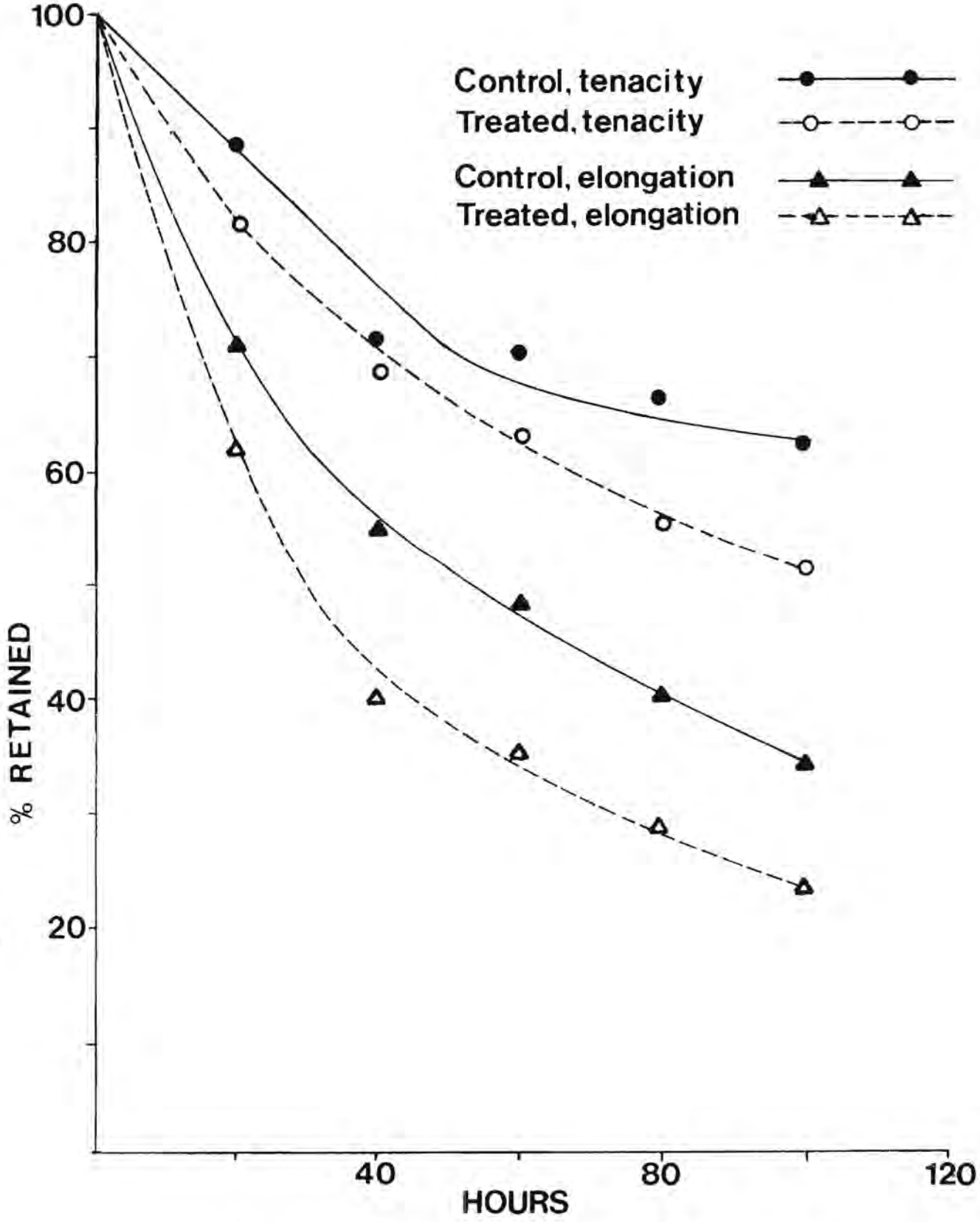

Figure 27. Retention of tenacity and elongation of Nomex Type 433 containing Irganox 1098 compared to control sample after carbon arc exposure.

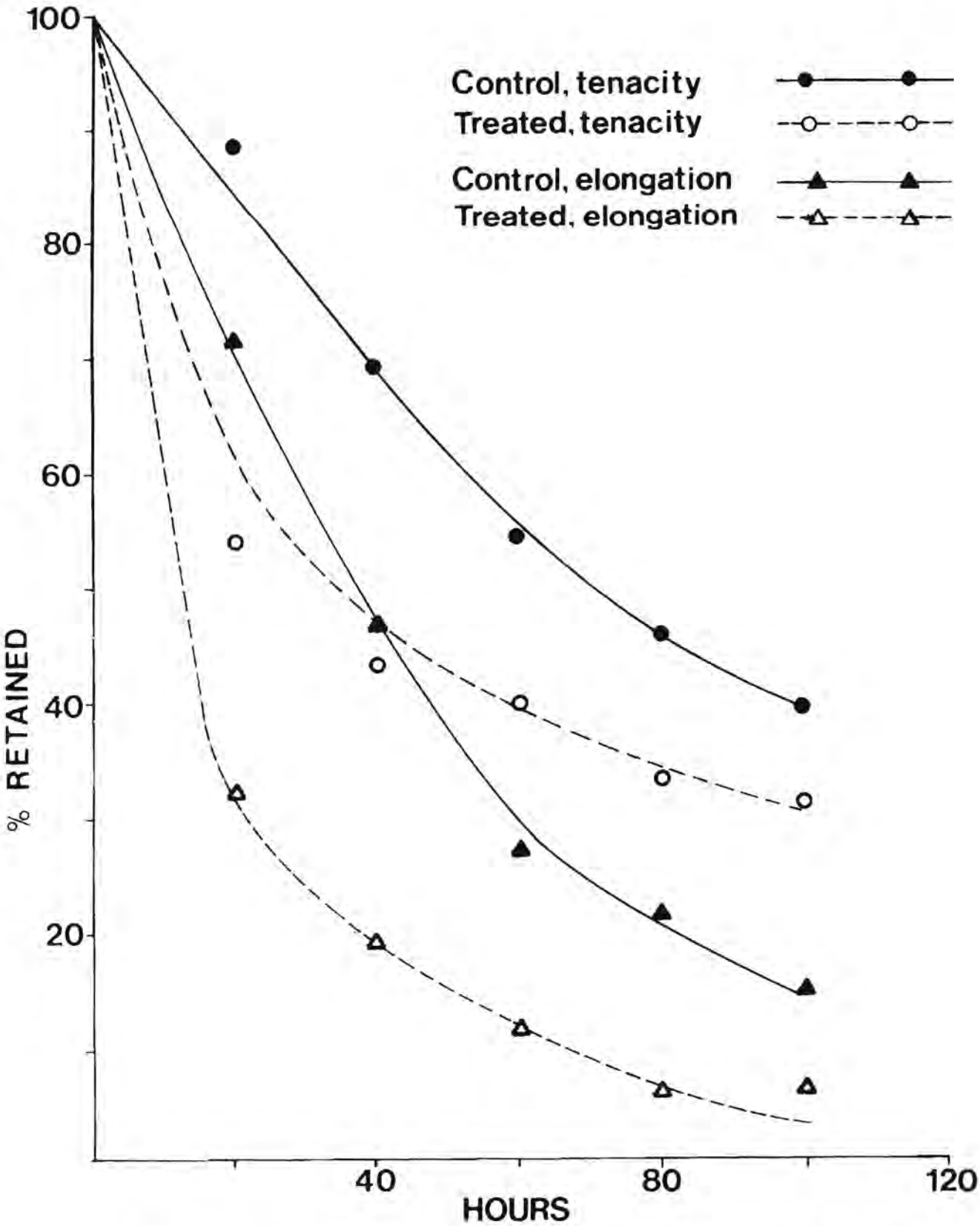

Figure 28. Retention of tenacity and elongation of Nomex Type 433 containing CGA-316 compared to control after carbon arc exposure.

Retention of tenacity and elongation for samples containing AM-105, IRGASTAB 2002, and Zetax are shown in Figures 29,30 and 31. All of the compounds containing nickel and zinc apparently reduce both the tenacity and elongation of Nomex on UV irradiation. This result was somewhat surprising in light of the reported favorable results with these stabilizers in other aromatic systems.

Results for Nomex yarn containing GI-IO-460 are shown in Figure 32. This is an experimental stabilizer produced by Ciba-Geigy and reported to be a substituted oxanilide. It had no significant effect on property retention of exposed Nomex yarn.

A similar result was observed for NBC, nickel dibutyldithiocarbamate as shown in Figure 33.

A second Ciba-Geigy experimental stabilizer CHA-1056 (Figure 34) appeared to adversely affect the stability of Nomex to UV degradation.

The quencher type stabilizers, as a group showed no improvements in the stabilization of Nomex to UV degradation.

5. Exposure Studies on Nomex Treated With Other Potential Stabilizers

Retention of tenacity and elongation on exposure to the carbon arc Fade-Ometer for samples containing urea are shown in Figure 35. The significant reduction in both properties by the presence of urea is obvious. Similar results for samples containing urea plus thiourea are shown in Figures 36. In this case almost no effect on properties is observed. Results for samples containing colloidal sulfur produced by reactions of acid and sodium thiosulfate are shown in Figure 37. No effects of the additive are noted in this case either. These findings suggest that compounds containing disulfide bonds are not stabilizers for Nomex.

The observation that urea adversely affects the properties of Nomex exposed to UV radiation was an interesting and unexpected result. It was felt that terminal $-NH_2$ groups in the polymer might be involved in the degradation mechanisms. Therefore, techniques to remove terminal $-NH_2$ groups by chemical reaction were explored.

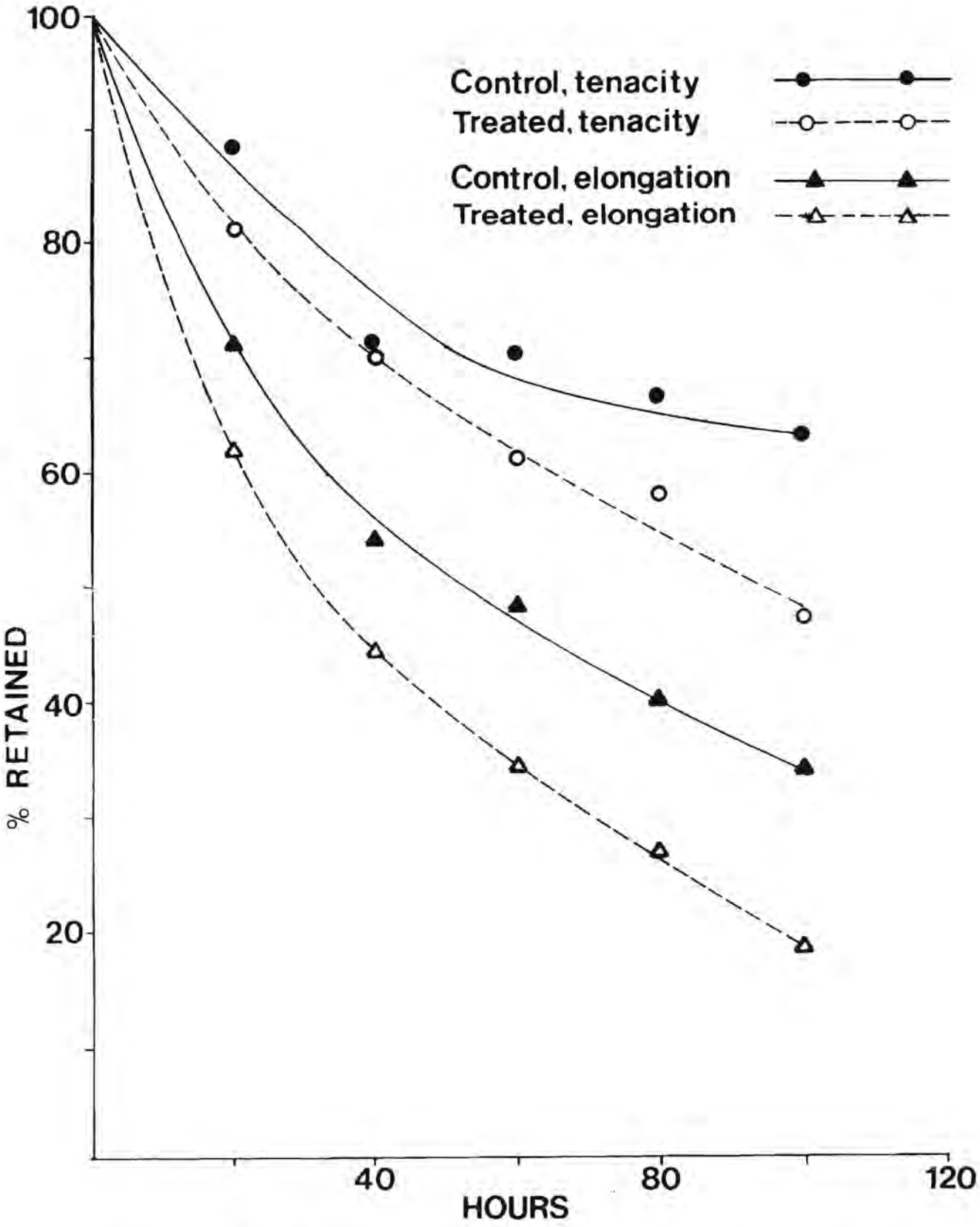

Figure 29. Retention of tenacity and elongation of Nomex Type 433 containing AM-105 compared to control after carbon arc exposure.

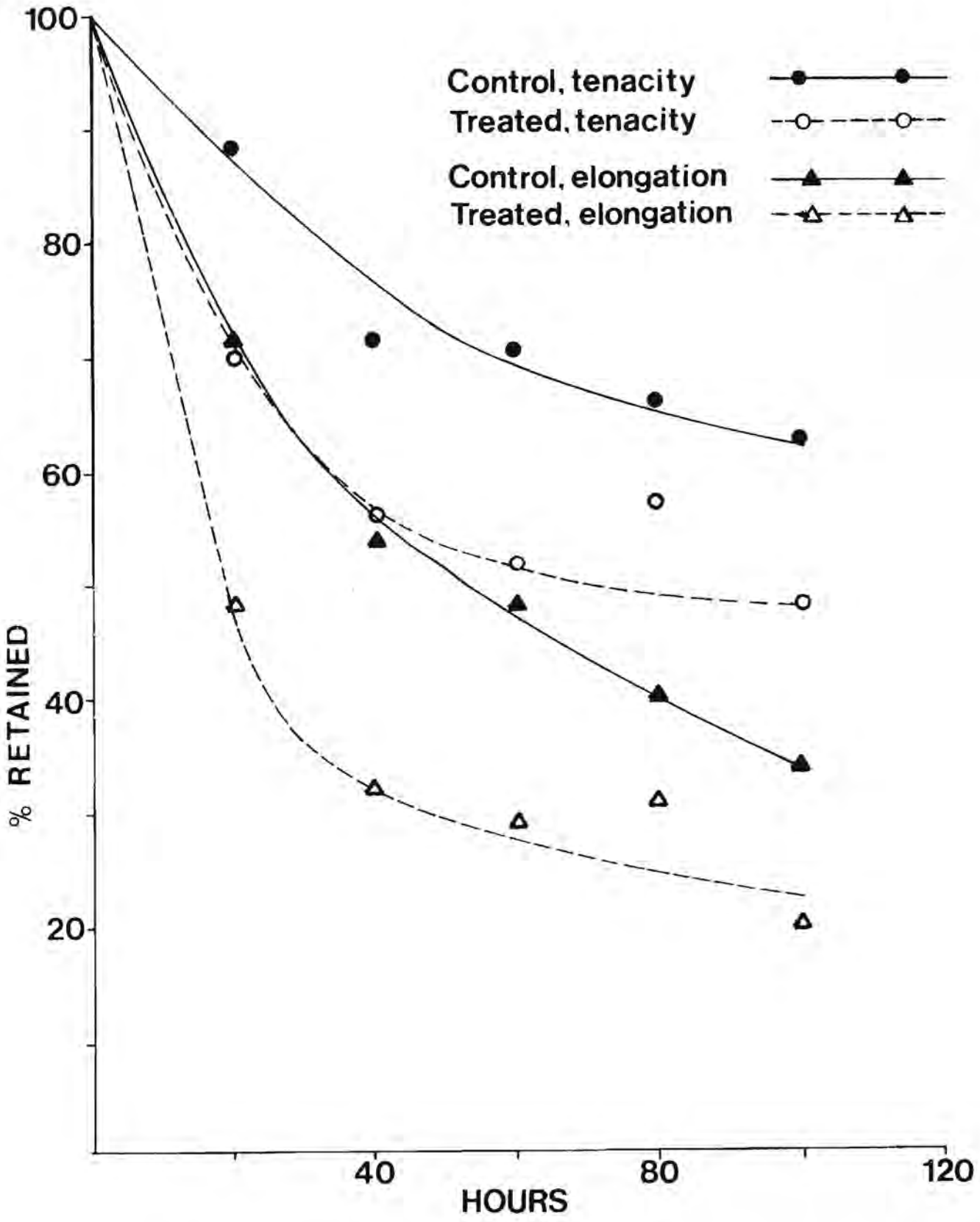

Figure 30. Retention of tenacity and elongation of Nomex Type 433 containing IRGASTAB 2002 compared to control after carbon arc exposure.

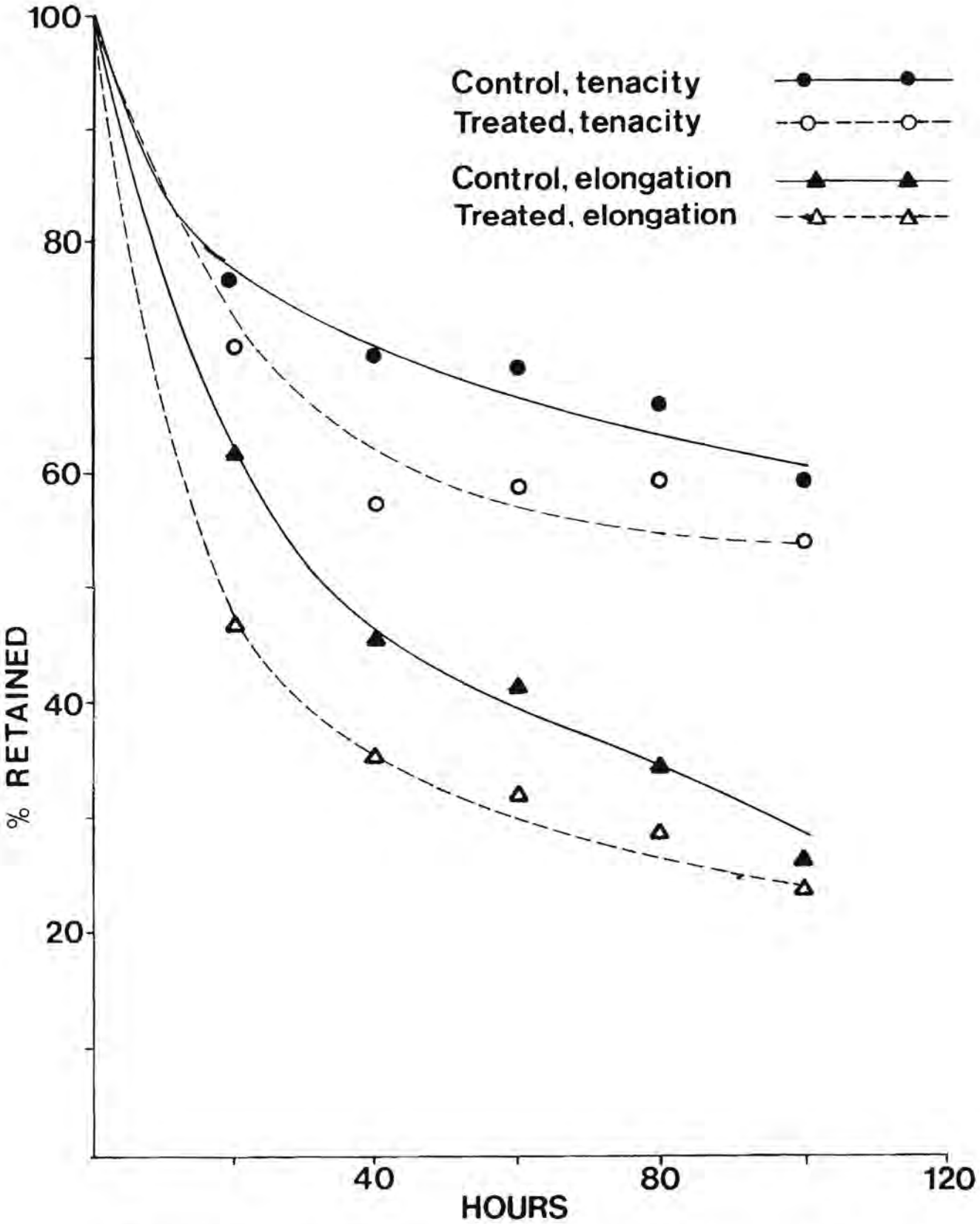

Figure 31. Retention of tenacity and elongation of Nomex Type 433 containing Zetax compared to control after carbon arc exposure.

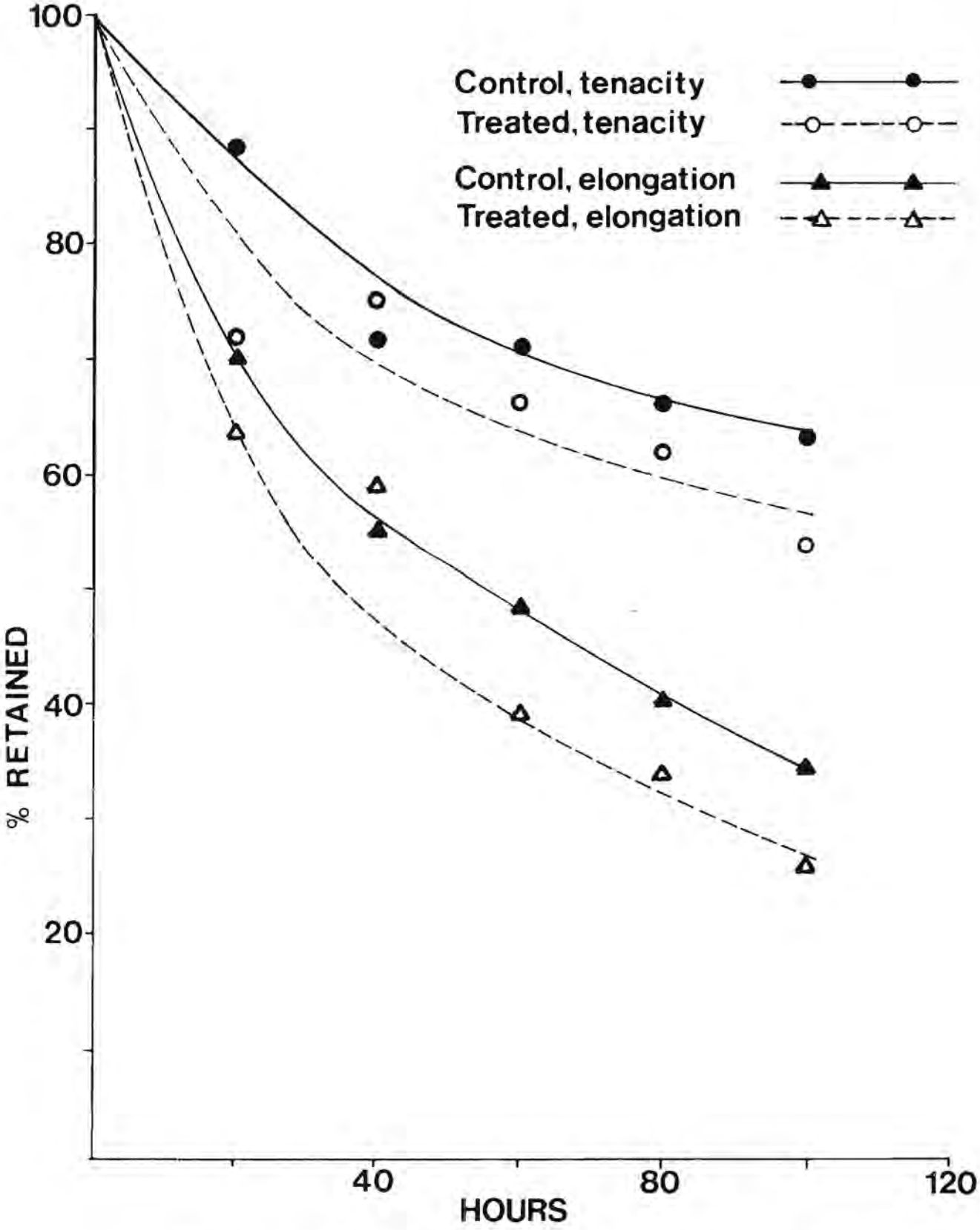

Figure 32. Retention of tenacity and elongation of Nomex Type 433 containing GI-10-460 compared to control after carbon arc exposure.

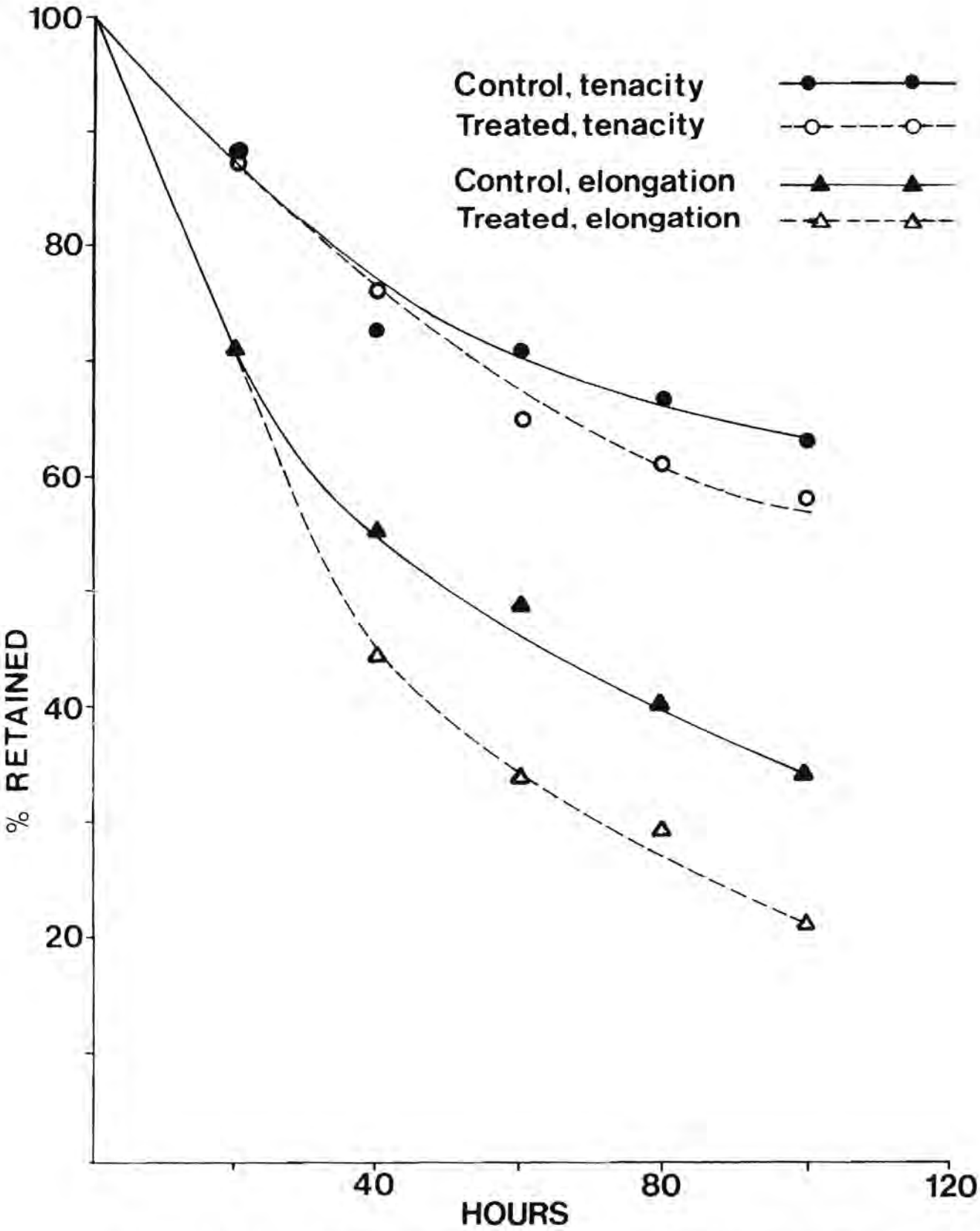

Figure 33. Retention of tenacity and elongation of Nomex Type 433 containing NBC compared to control after carbon arc exposure.

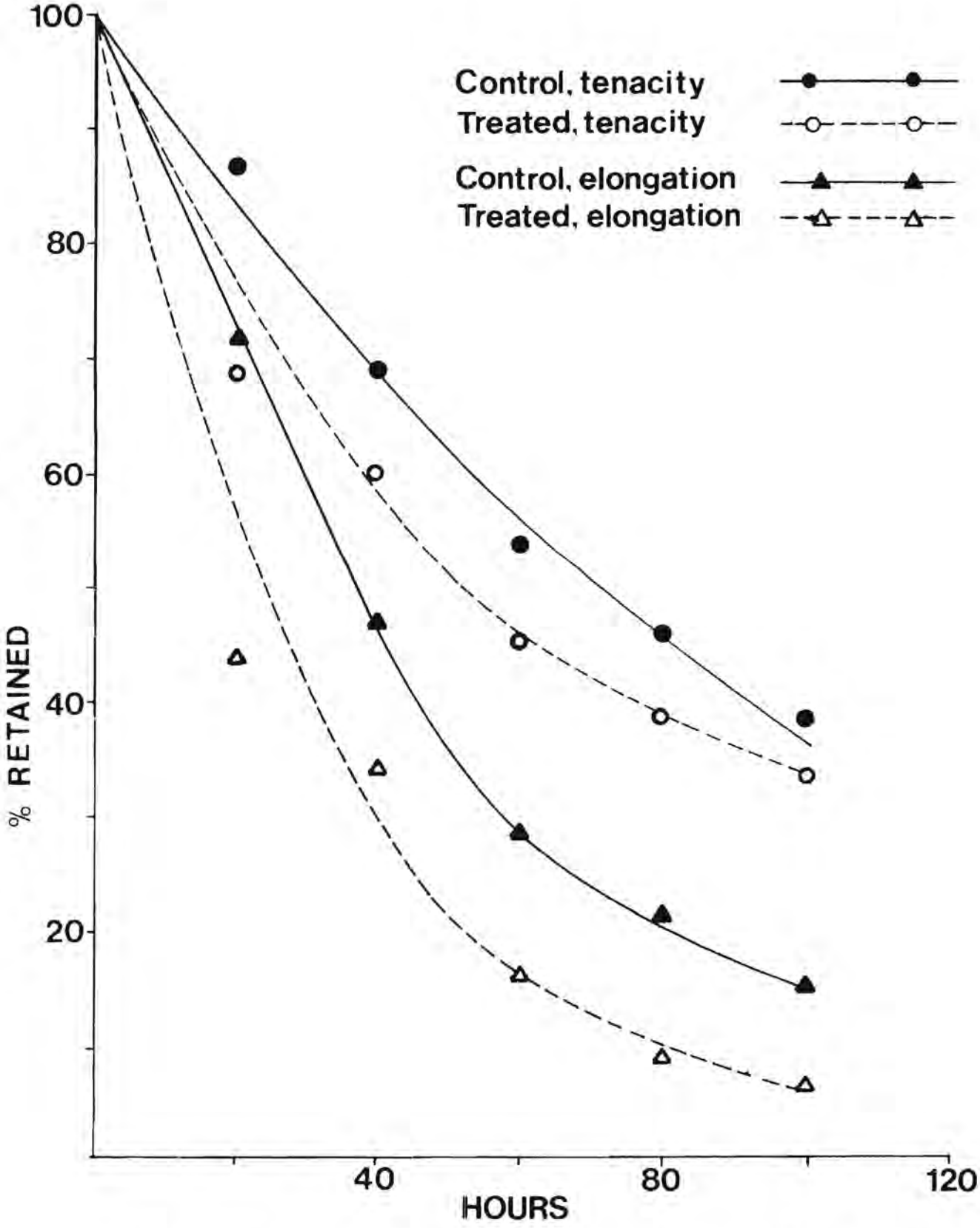

Figure 34. Retention of tenacity and elongation of Nomex Type 433 containing CHA-1056 compared to control after carbon arc exposure.

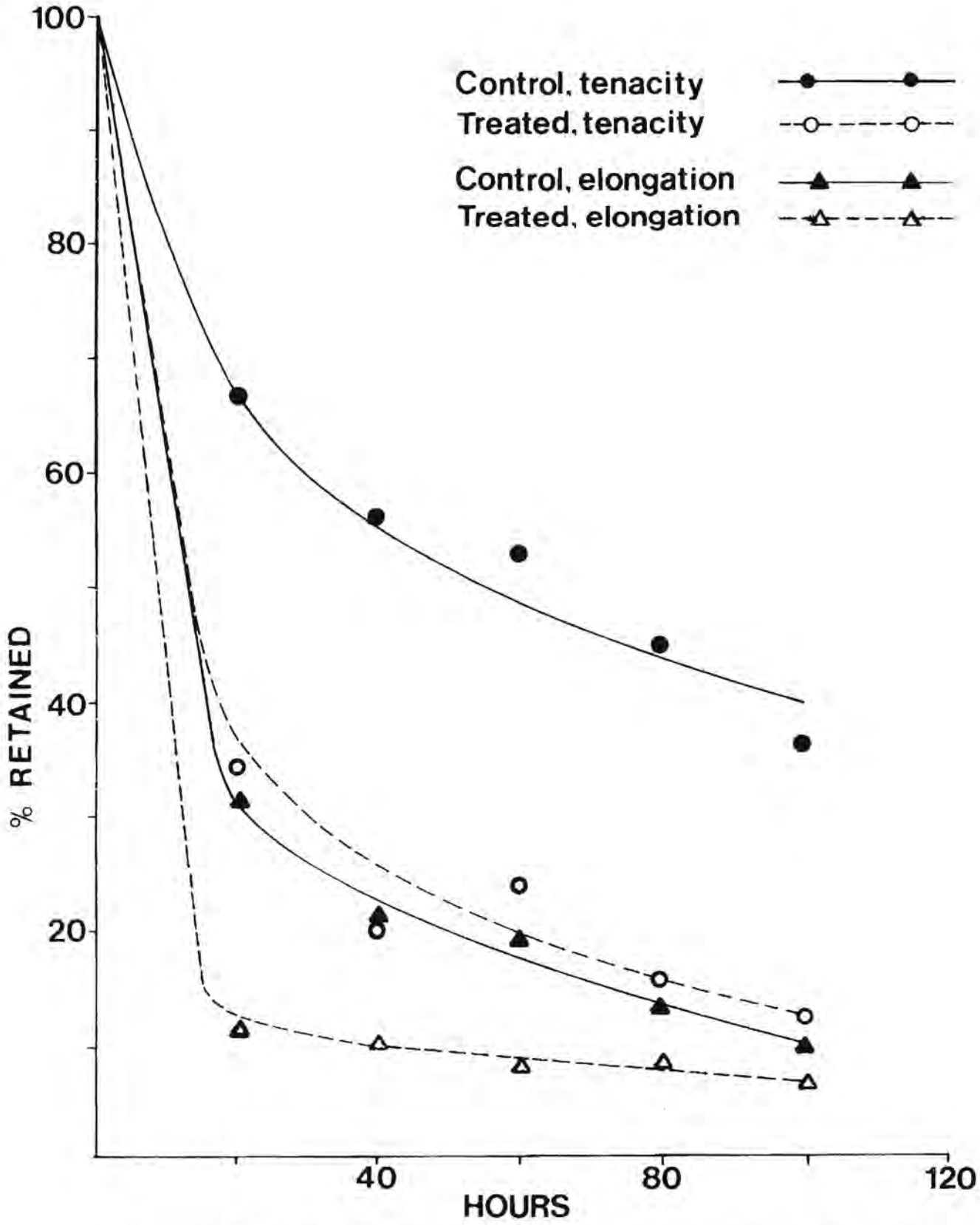

Figure 35. Retention of tenacity and elongation of Nomex Type 430 containing urea compared to control after carbon arc exposure.

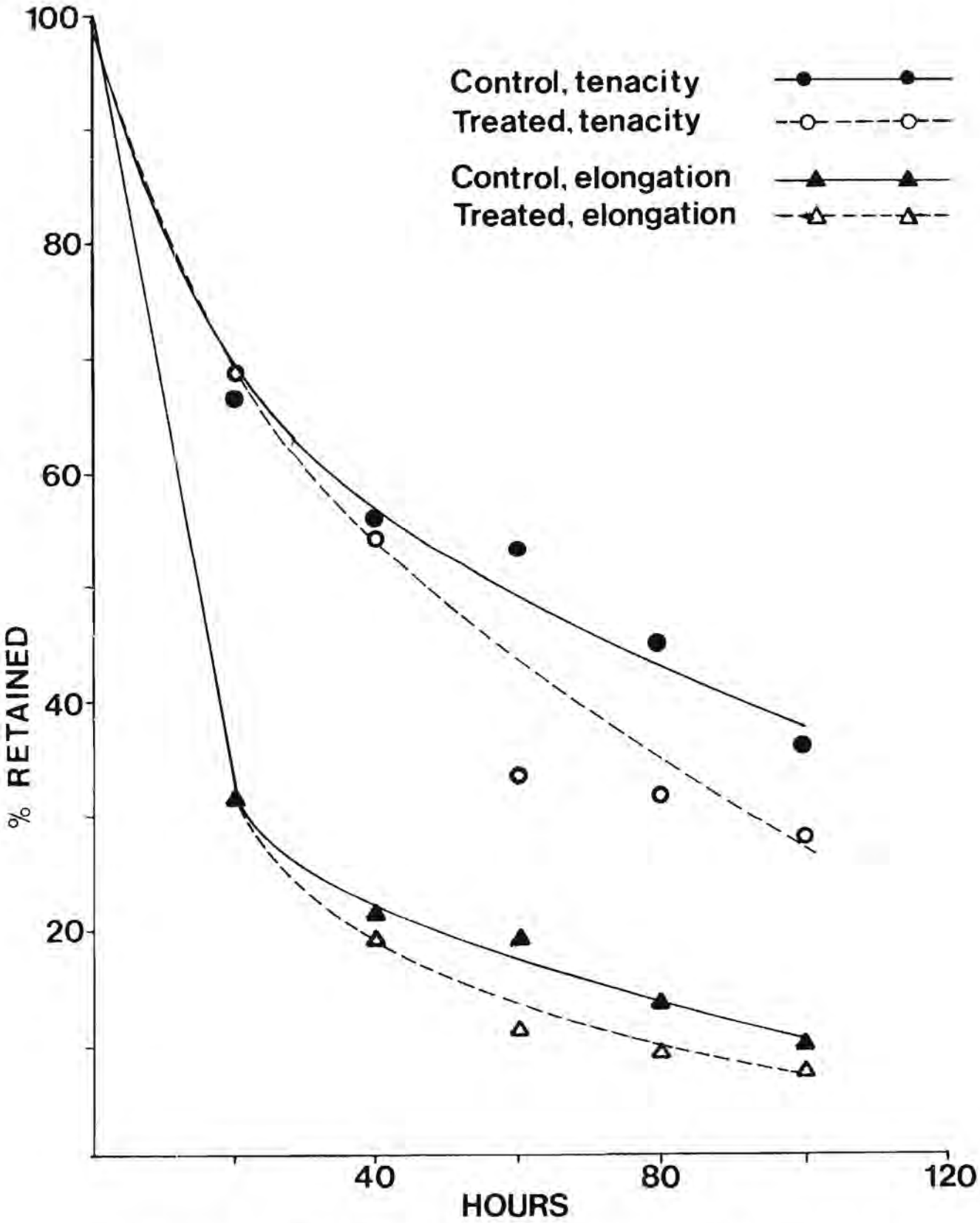

Figure 36. Retention of tenacity and elongation of Nomex Type 430 containing urea and thiourea compared to control after carbon arc exposure.

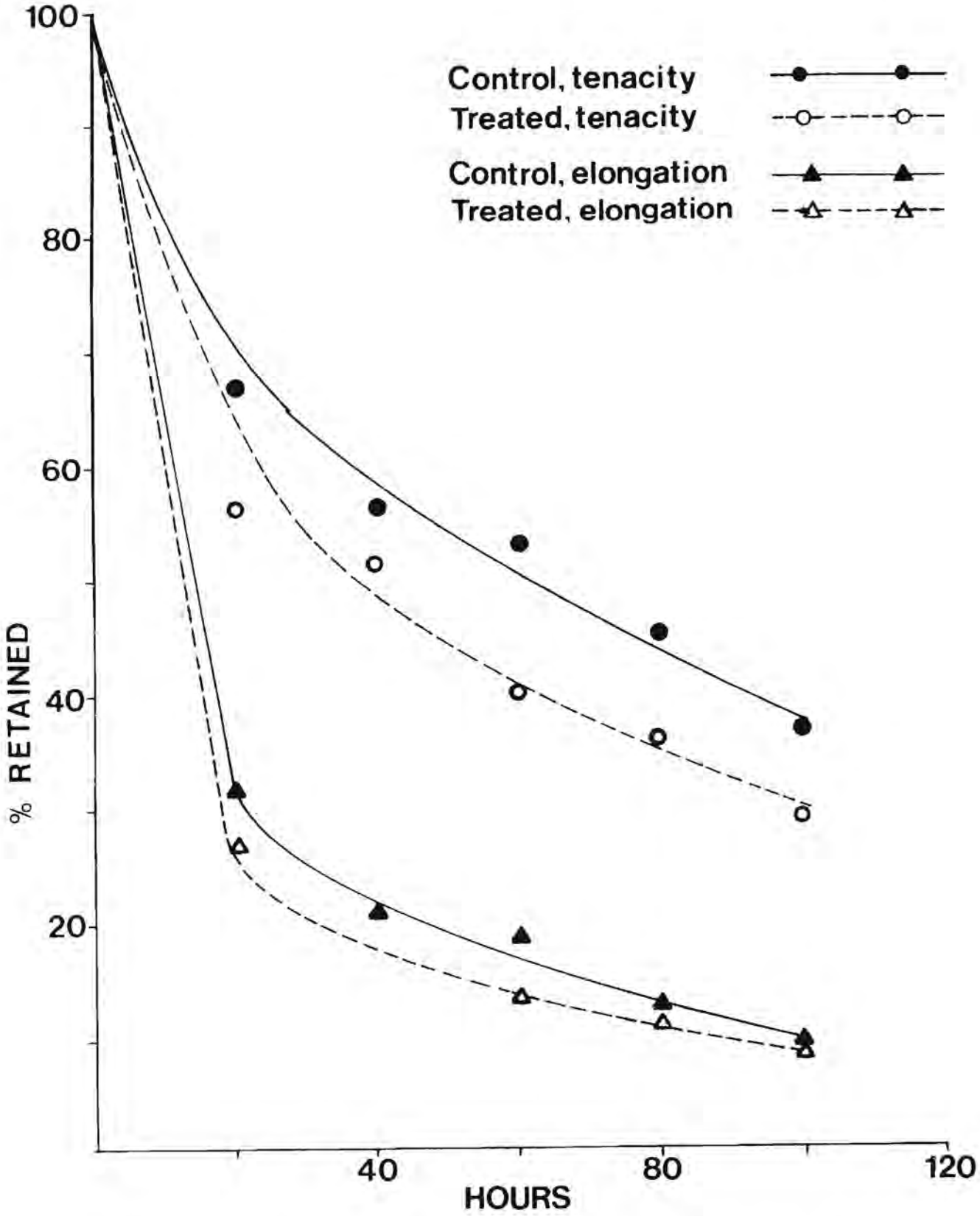

Figure 37. Retention of tenacity and elongation of Nomex Type 430 containing colloidal sulfur compared to control after carbon arc exposure.

Aromatic amines in the presence of nitrous acid react to form diazonium salts which readily react with phenols to produce diazo compounds. These reactions are used extensively in preparation of the diazo class of dyestuffs and were used to reduce the number of amine end groups in a sample of Nomex yarn.

The yarn samples were first treated with nitrous acid in the presence of a carrier. They were then treated with beta-oxynaphthoic acid. Formation of the colored diazo compound gave evidence that the aromatic amine end groups were undergoing reaction.

Samples with reacted amine end groups were exposed to the carbon arc Fade-Ometer and compared with control samples. Results are shown in Figure 38. These results suggest that reduction in amine end group content does not provide greater stability to Nomex yarn.

The only other potential stabilizer giving evidence of stabilizing Nomex against UV degradation was oxanilide. Retention of tenacity and elongation after 100 hour exposure to the carbon arc is shown in Figure 39. Oxanilide appears to give significant improvement in tenacity. Retention of elongation is not appreciably affected. Oxanilide was selected for further study.

G. Studies on DuPont E-11 Fabrics

Two of the effective stabilizers, Tinuvin P and Blancophor AW, were also applied to a new experimental thermally stable fabric designated E-11. Results of these studies are presented in Appendix B.

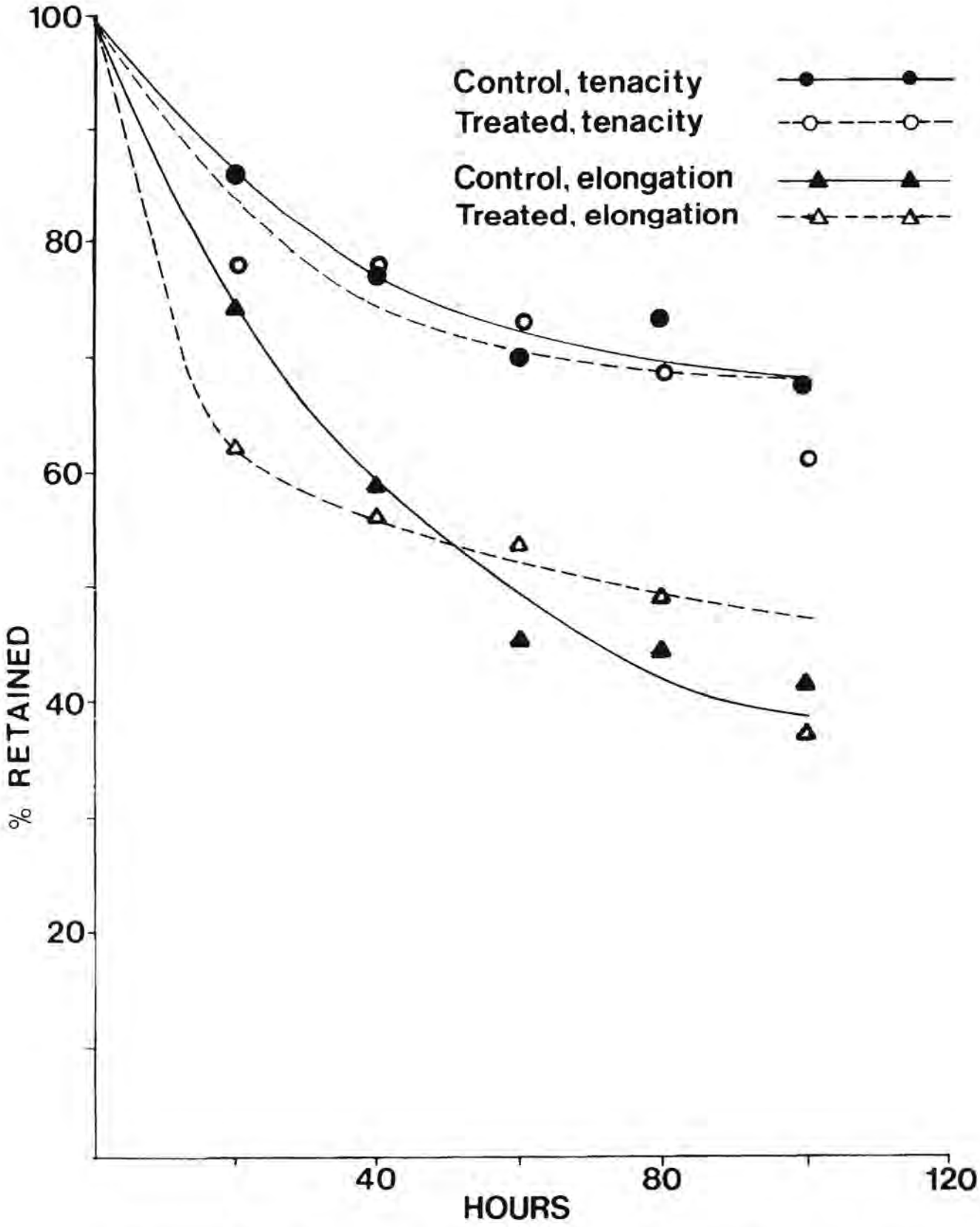

Figure 38. Retention of tenacity and elongation of Nomex Type 433 with end groups reacted with beta-oxynaphthoic acid compared to control after carbon arc exposure.

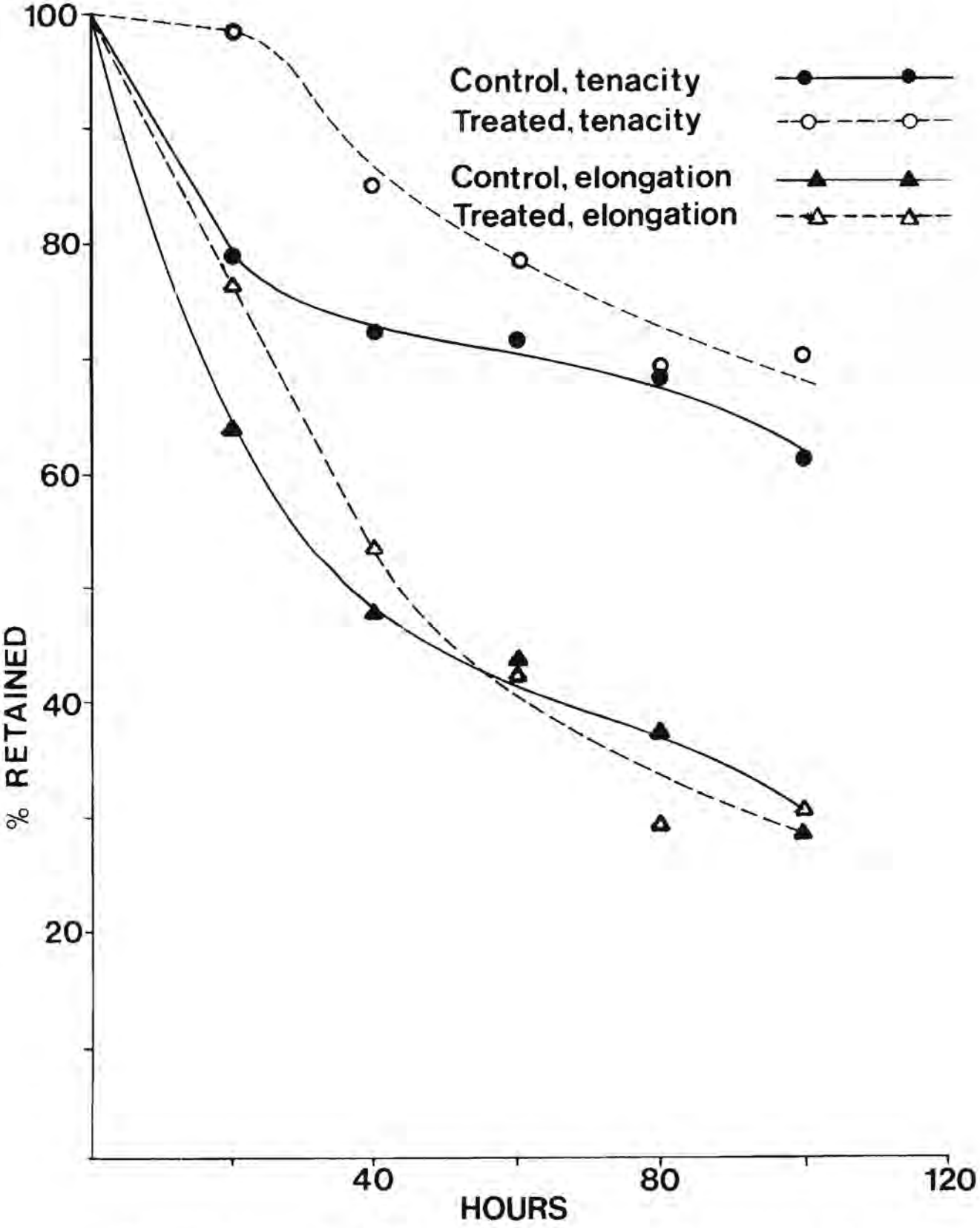

Figure 39. Retention of tenacity and elongation of Nomex Type 433 containing oxanilide compared to control after carbon arc exposure.

SECTION III

DEVELOPMENT OF STABILIZER SYSTEMS

A. Factorial Experiment

Based on the stabilizer screening studies, three compounds were selected for further study -- Blancophor AW, Tinuvin P, and oxanilide.

Blancophor AW is a commercially available optical brightener of the aminocoumarin type produced by GAF. Of the three compounds, Blancophor AW appeared to have the most beneficial effect on Nomex light stability. In all experiments conducted Blancophor AW increased retention of both tenacity and elongation of Nomex yarn.

Tinuvin P is a UV screening agent of the benzotriazole type produced by the Ciba-Geigy Company. It has been reported to be a stabilizer for Nomex but the results have not been consistent. In addition to being a strong UV absorber, it has been suggested that Tinuvin P may also act as a quencher of excited states.

Oxanilide is the diamide produced by reaction of oxalic acid with aniline. It is sometimes used as a "copper inhibitor" in stabilizer formulations for polymers. A variety of mechanisms have been suggested to explain the stabilizing action of oxanilide including the quenching of excited states and UV absorption. The mechanism by which oxanilide stabilizes Nomex is not known at the present time.

A factorial experiment was carried out to investigate the three selected stabilizers at 4 concentration levels (0,33,66, and 100% o.w.f.) on Nomex sage green fabric (Mil-C-38351,Type II,Class 1) to establish optimum concentrations for stabilization and to determine if synergistic effects are present. The experimental plan and the order in which the experiments were conducted as given in Table 2.

Results of initial exposure experiments on the Nomex fabric are shown in Figures 40 and 41. Samples of fabric were exposed for 0,20,40,60,80 and 100 hours and strength and elongation determined in the warp and fill orientation by the 1" ravel strip test. In both carbon arc and xenon arc exposure the loss in breaking strength and elongation

TABLE 2

FACTORIAL FOR SELECTION OF STABILIZER SYSTEMS

Experiment No.	Sample*
1	$A_3B_1C_1$
2	$A_3B_1C_3$
3	$A_2B_2C_2$
4	$A_2B_2C_2$
5	$A_1B_3C_1$
6	$A_1B_1C_1$
7	$A_3B_3C_1$
8	$A_1B_3C_3$
9	$A_3B_3C_3$
10	$A_1B_1C_3$
11	$A_0B_0C_0$

* A = Blancophor AW

B = Tinuvin P

C = Oxanilide

0 = 0 % OWF

1 = 33 % OWF

2 = 66 % OWF

3 = 100% OWF

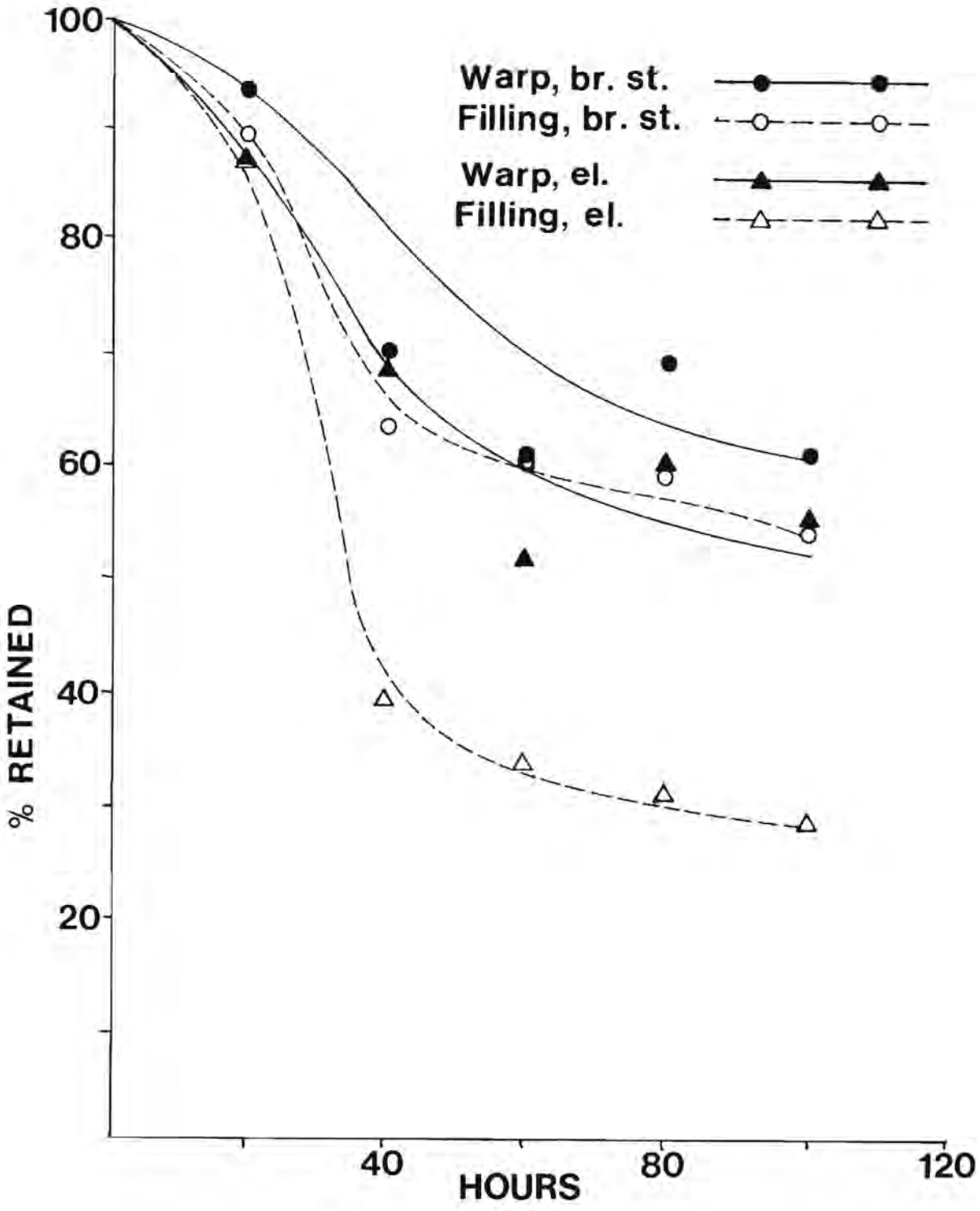

Figure 40. Retention of breaking strength and elongation of Nomex fabric exposed in the carbon arc Fade-Ometer.

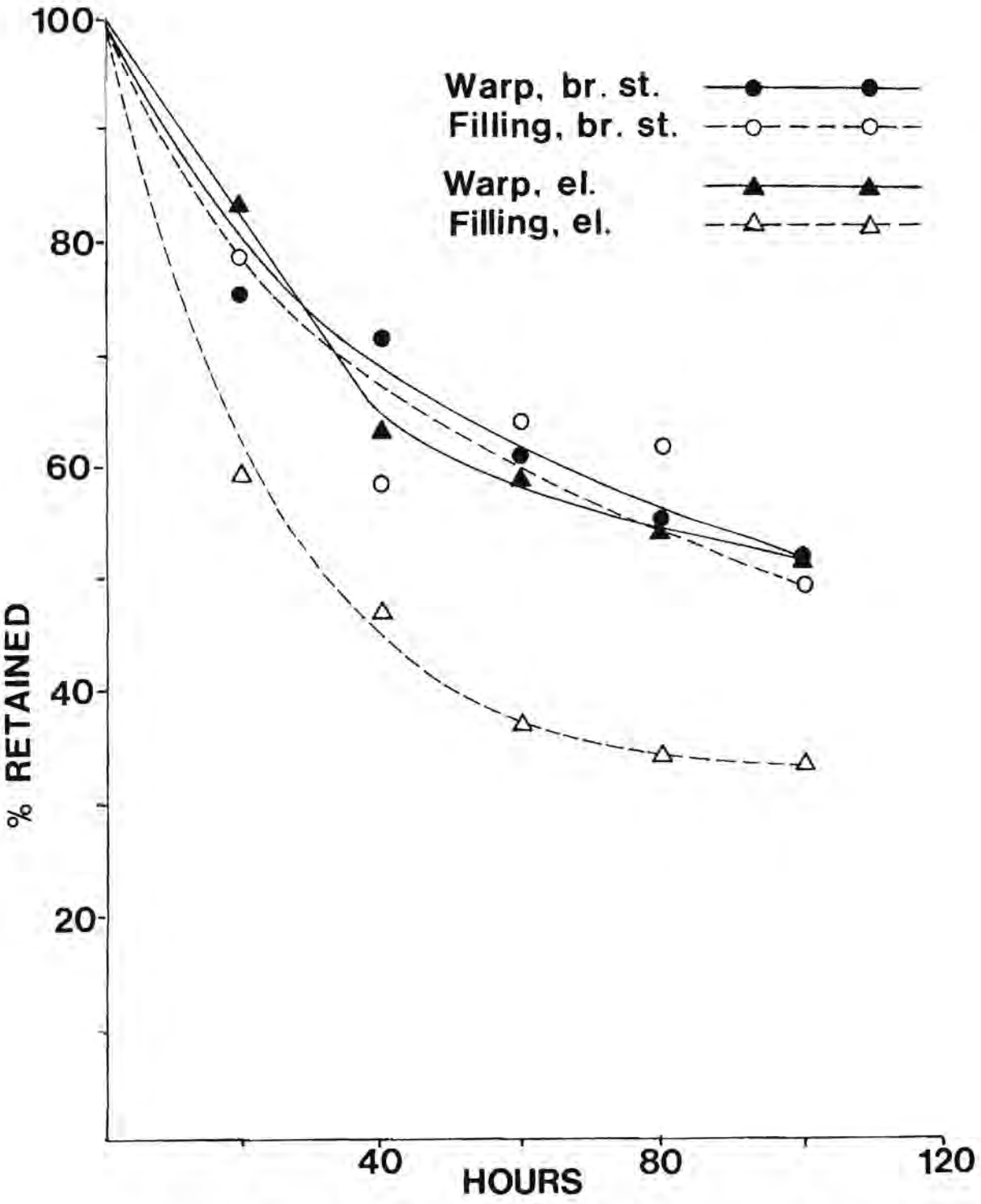

Figure 41. Retention of breaking strength and elongation of Nomex fabric exposed in the xenon arc Fade-Ometer.

in the warp direction and the loss of breaking strength in the filling direction follow very similar curves. The elongation in the filling direction decreases more sharply on exposure. In subsequent experiments changes in properties in the warp direction on exposure were determined as this is the direction subjected to greatest stress in end-use applications of Nomex fabric.

Results of the central composite design experiment for testing three stabilizers (Blancophor AW, Tinuvin P, and Oxanilide) at four concentration levels (0%,33%,66% and 100%) are shown in Table 3. Results are reasonably consistent with a few exceptions. Several samples at the 60 hour exposure time ($A_3B_1C_1$, $A_3B_1C_3$) show unusually low strengths. Data at 80 and 100 hours for these samples suggest that some problem of undetermined origin is responsible for the low values at the 60 hour exposure time. Sample $A_1B_3C_1$ shows extremely high values for the strength both initially and after all exposure times. The reason for these unusually high values is not apparent.

TABLE 3

AVERAGE STRENGTH MEASURED AT VARIOUS UV EXPOSURE LEVELS FOR ALL TREATMENT COMBINATIONS

Treat. Comb.	Average Strength (Pounds) After Exposure					
	0	20	40	60	80	100
$A_0B_0C_0$	224	198	170	160	159	146
$A_1B_1C_1$	244	219	213	199	199	197
$A_1B_1C_3$	234	192	182	186	205	213
$A_1B_3C_3$	221	240	224	212	201	198
$A_3B_1C_1$	212	184	203	127	162	218
$A_3B_1C_3$	215	205	178	117	180	191
$A_3B_3C_3$	229	230	215	183	207	207
$A_1B_3C_1$	270	260	230	233	227	229
$A_3B_3C_1$	222	229	205	202	217	193
$A_2B_2C_2$	203	217	218	219	220	221

95% Confidence Limit = $\pm$ 14 lbs.

$A_0B_0C_0$ - UV inhibitors not present

$A_1B_1C_1$ - UV inhibitors present in lowest concentrations

$A_3B_3C_3$ - UV inhibitors present in highest concentrations

The effects of concentration of the three stabilizers on UV stability of Nomex fabrics are shown in Figures 42,43 and 44. The strength after both 40 and 100 hours exposure for samples containing Blancophor AW (Figure 42) suggest that little improvement in strength retention occurs above 33%. In fact there is some indication that higher levels may actually give less strength retention than the 33% level. Similiar results were obtained for Oxanilide as shown in Figure 44. The drop in strength at higher concentration was somewhat more pronounced in this case.

Tinuvin P does not reach maximum effectiveness until approximately 50% OWF is present in the dyebath. There is little difference in strength at the 67 and 100% level (see Figure 43).

The lack of data between 0 and 33% for all additives at least suggested the possibility that lower levels might be as effective as 33%. A sample was prepared, therefore, with 10% of each of the additives in the dyebath. The results for this sample is shown as the dotted circle and circled x in Figures 42 - 44.

Interactive effects between the stabilizer candidates are shown in Figure 45 - 50. No pronounced effects are observed between the various components. In general, high levels of B in combination with low levels of A and C gave somewhat higher strengths.

Another important observation made during the factorial experiment was that the Blancophor AW reduced the dye lightfastness of the sage green fabric. The color change was somewhat more pronounced than the change observed for the sage green fabric with no additions.

Based on the results of the factorial experiment, four stabilizer systems were selected for in-depth investigation. From Figures 42 and 44, it appears reasonable that levels of Blancophor AW and Oxanilide above 33% (owf) do not contribute appreciably to the retention of tensile strength on UV exposure. Similarly, levels of Tinuvin P above 50% (owf) are probably not beneficial.

A number of criteria were used in selection of the stabilizer systems. First, the lowest levels expected to be effective were selected to reduce treatment costs and give lower add-on of chemicals which may adversely affect other properties of the fabric. Second, at least two

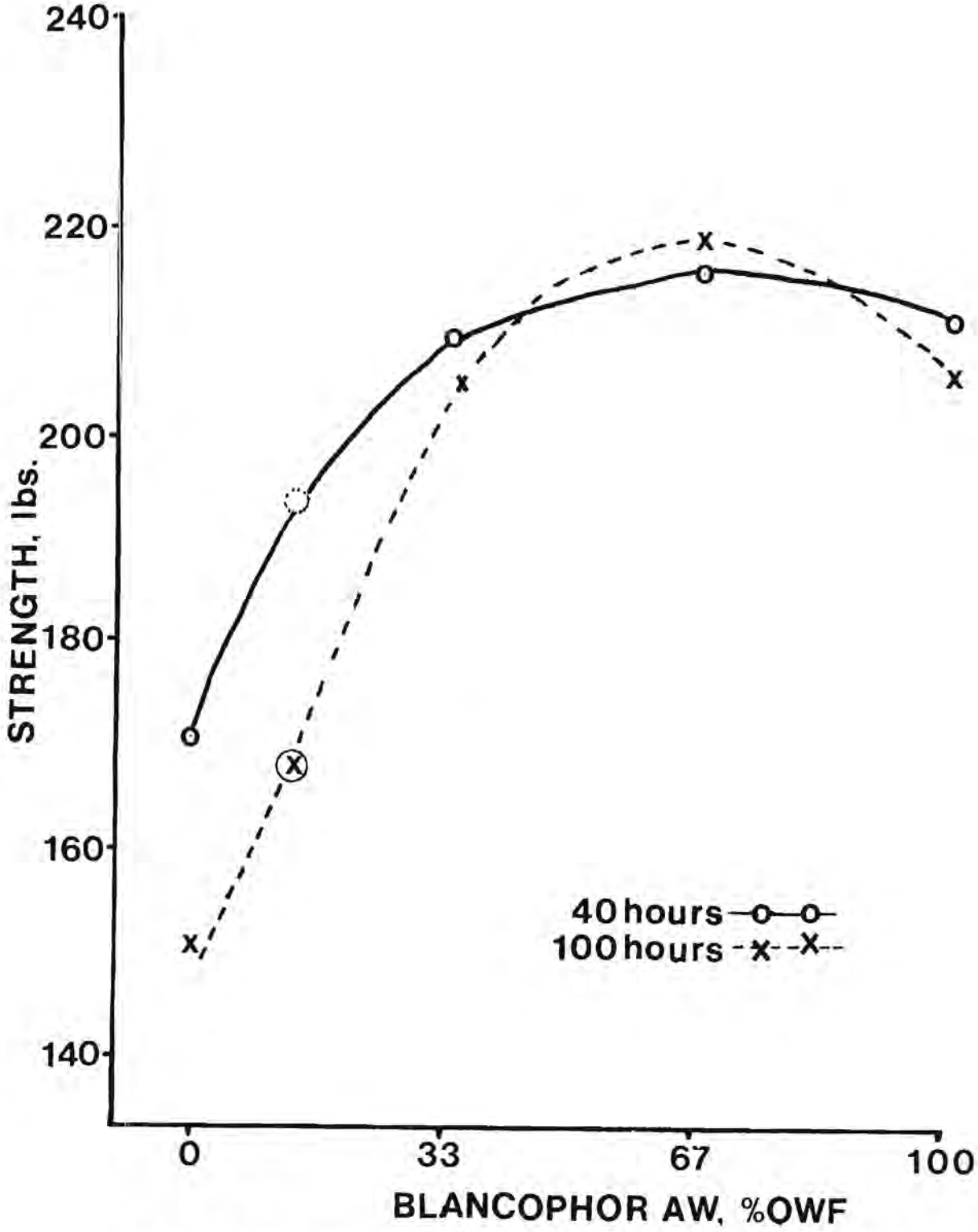

Figure 42. The effect of concentration of Blancophor AW on strength of Nomex fabrics after exposure for 40 and 100 hours in the carbon arc Fade-Ometer.

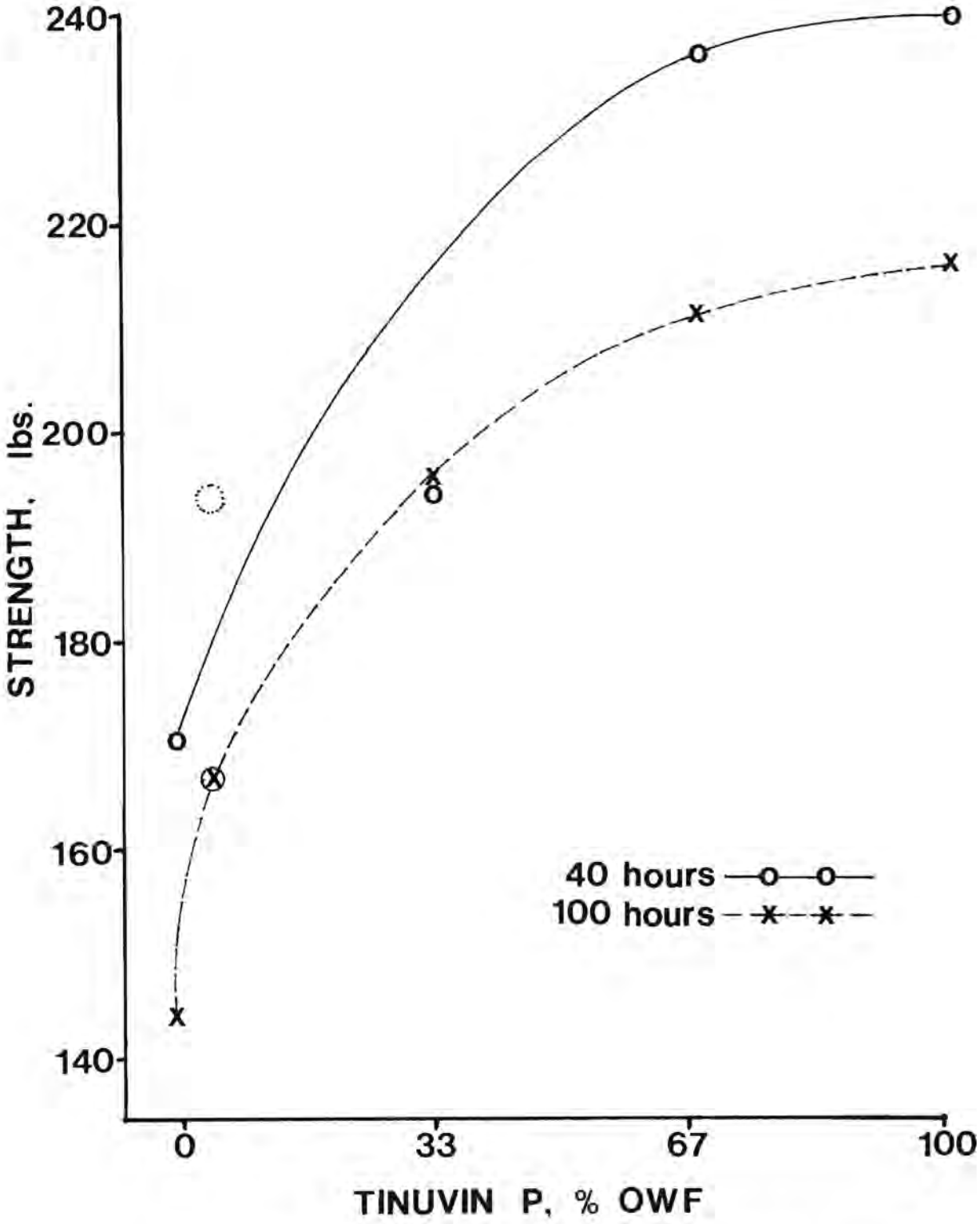

Figure 43. The effect of concentration of Tinuvin P on strength of Nomex fabrics after exposure for 40 and 100 hours in the carbon arc Fade-Ometer.

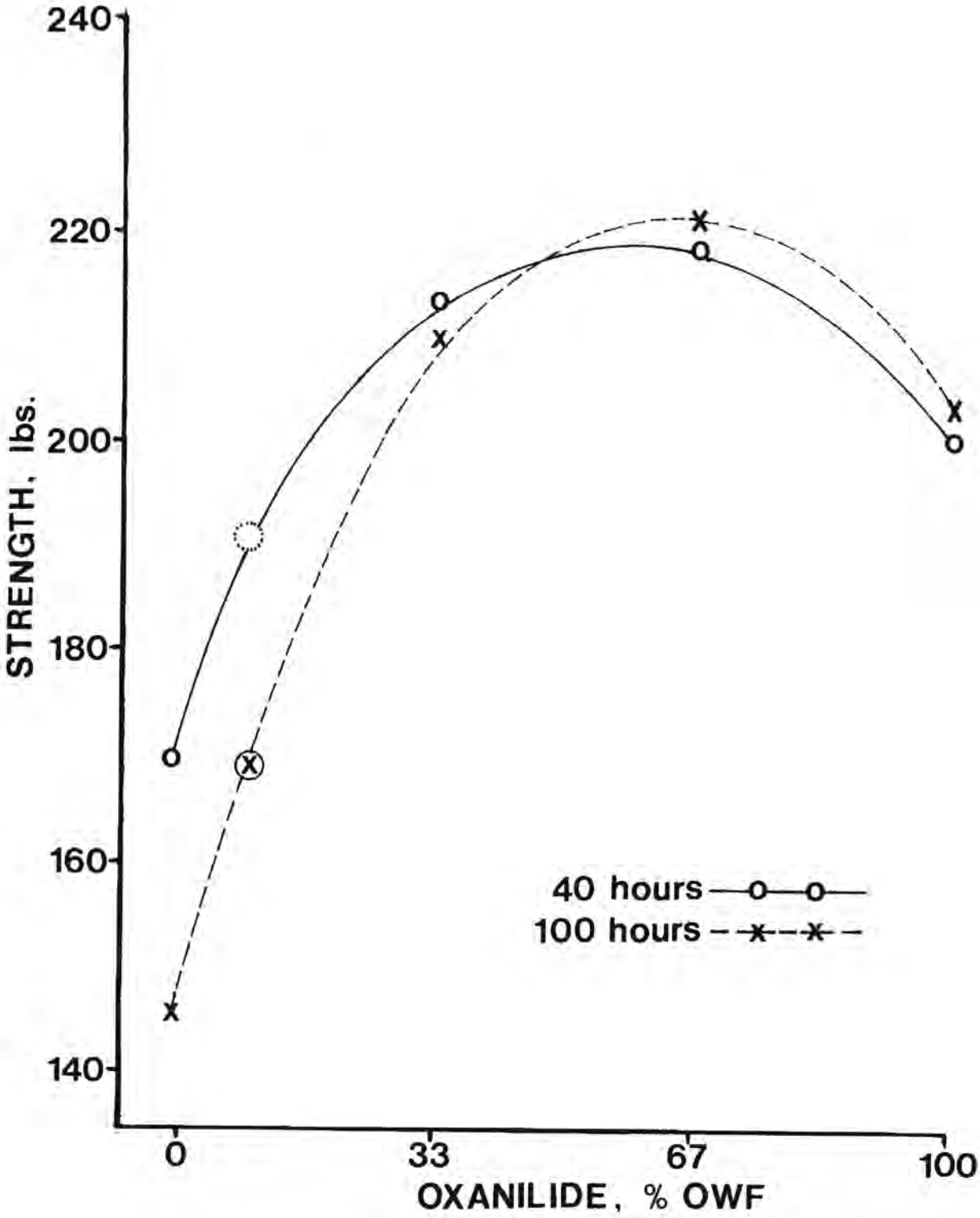

Figure 44. The effect of concentration of oxanilide on strength of Nomex fabrics after exposure for 40 and 100 hours in the carbon arc Fade-Ometer.

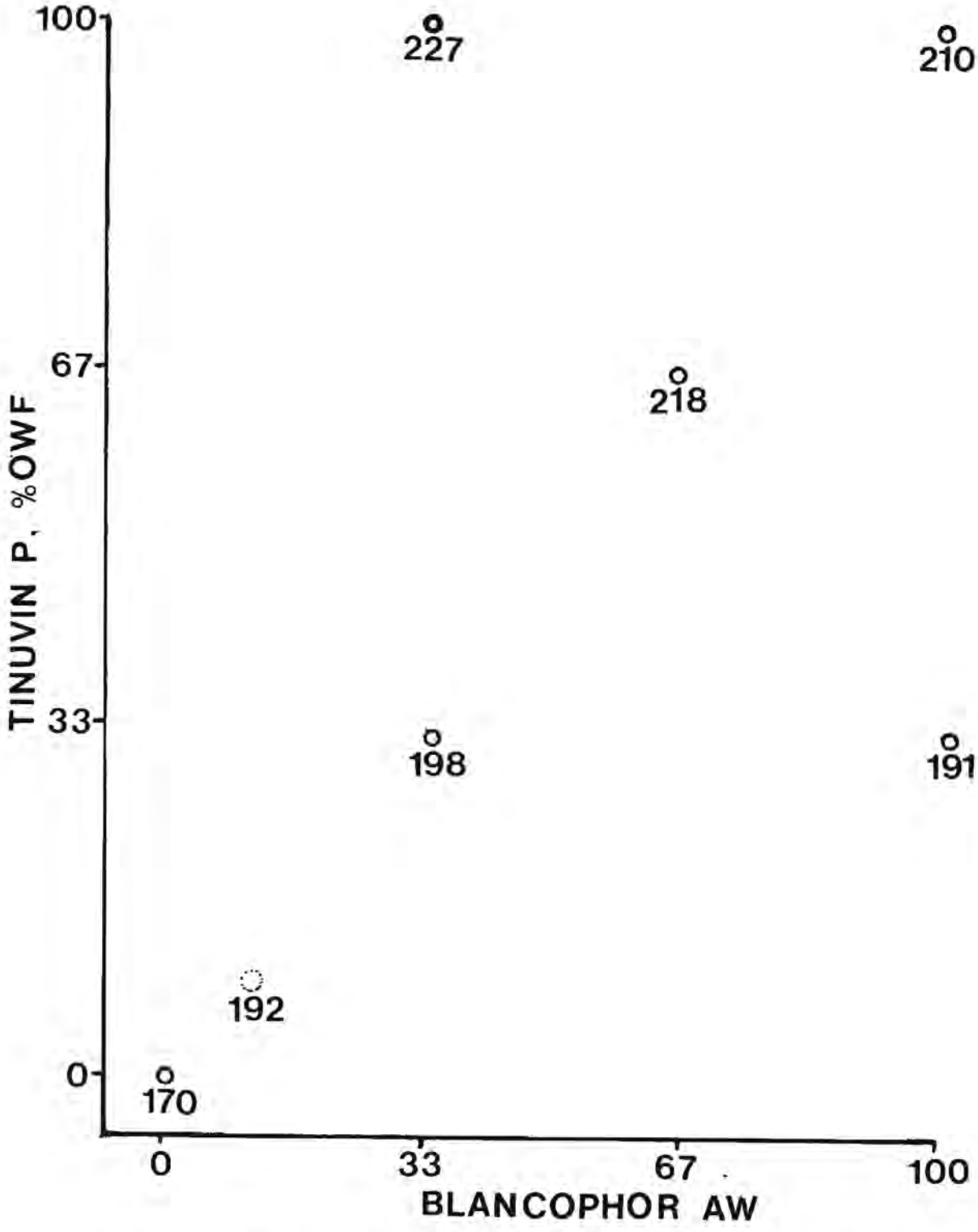

Figure 45. Strength after 40 hours exposure of fabric samples containing Blancophor AW and Tinuvin P.

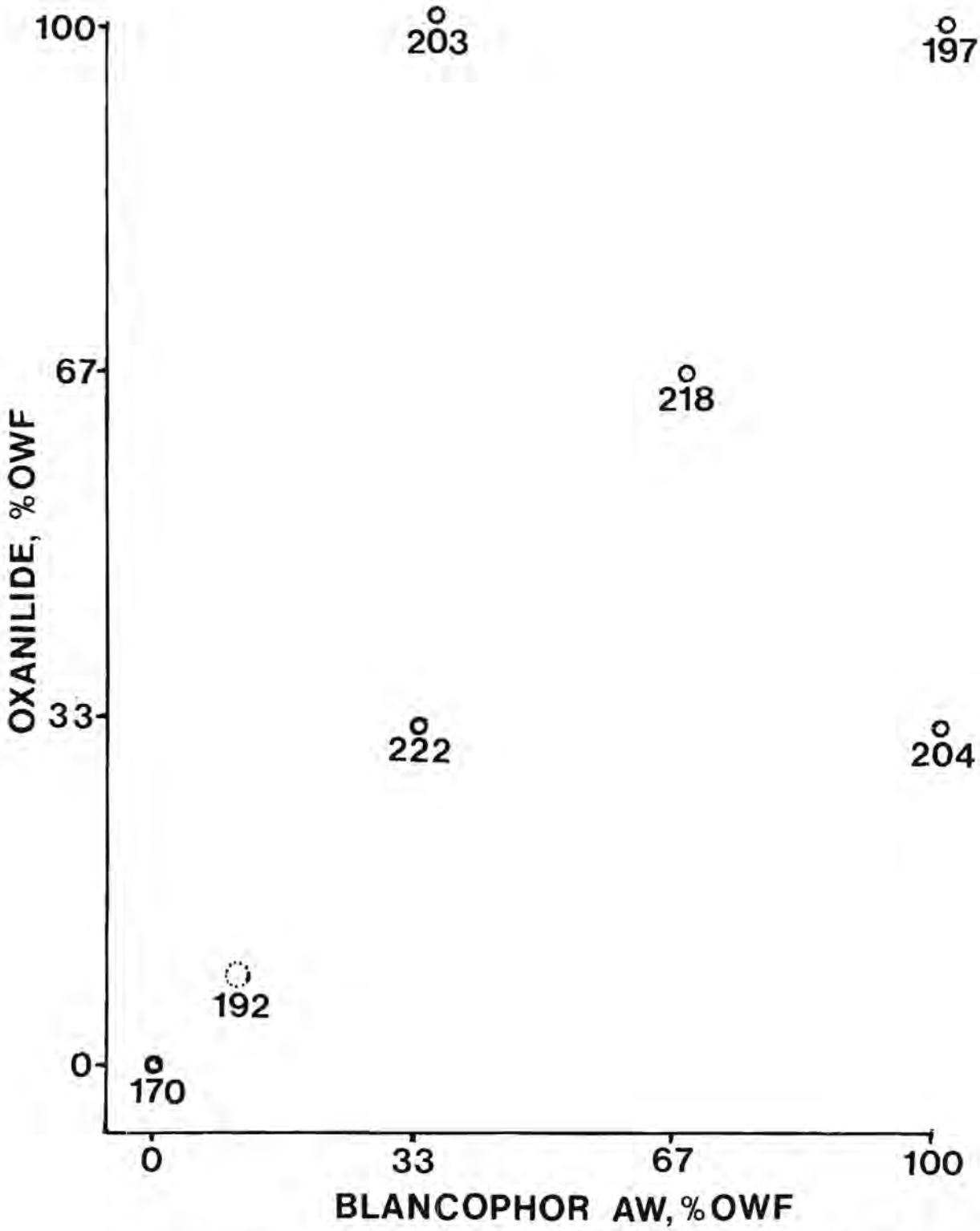

Figure 46. Strength after 40 hours exposure of fabric samples containing oxanilide and Blancophor AW.

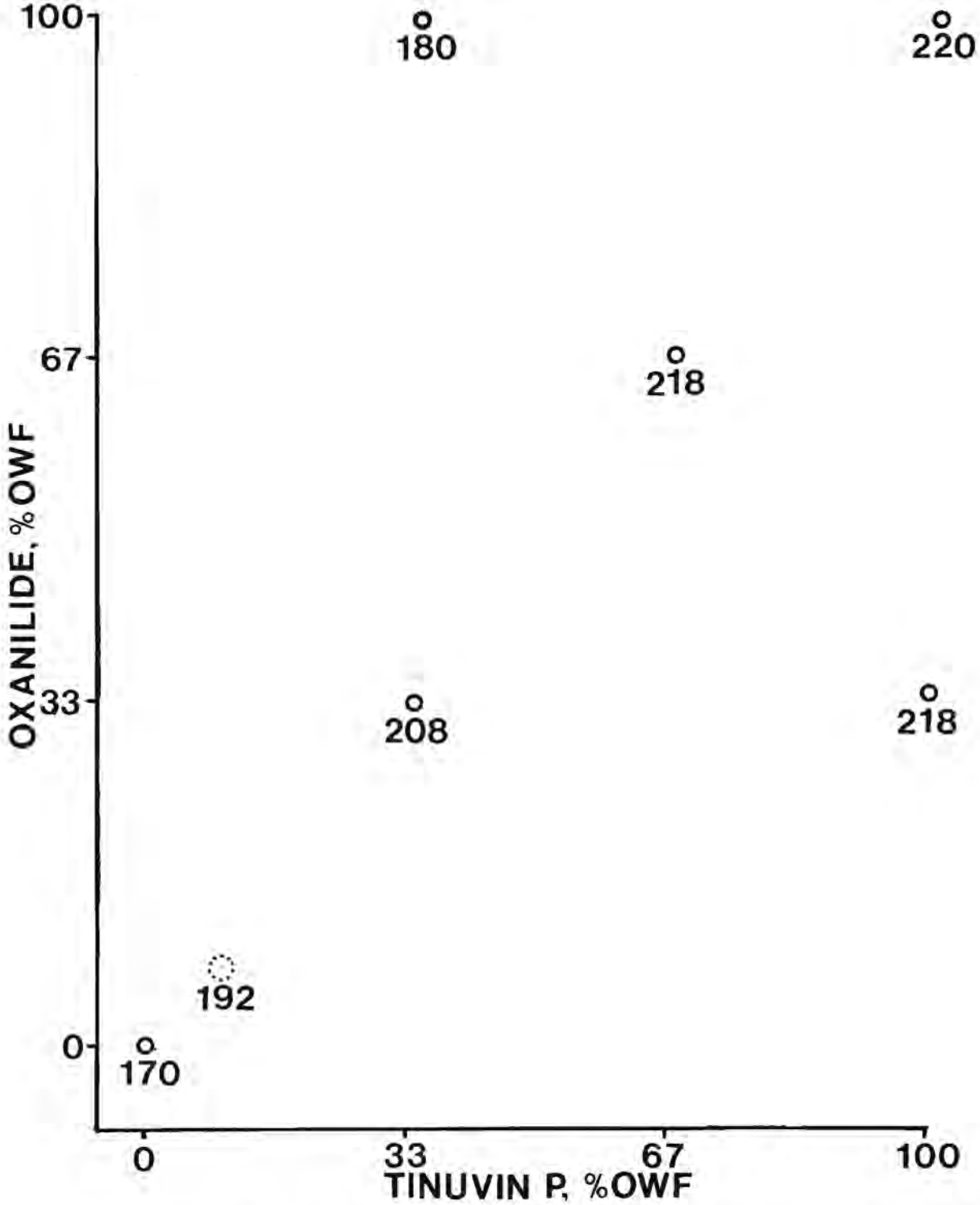

Figure 47. Strength after 40 hours exposure of fabrics samples containing oxanilide and Tinuvin P.

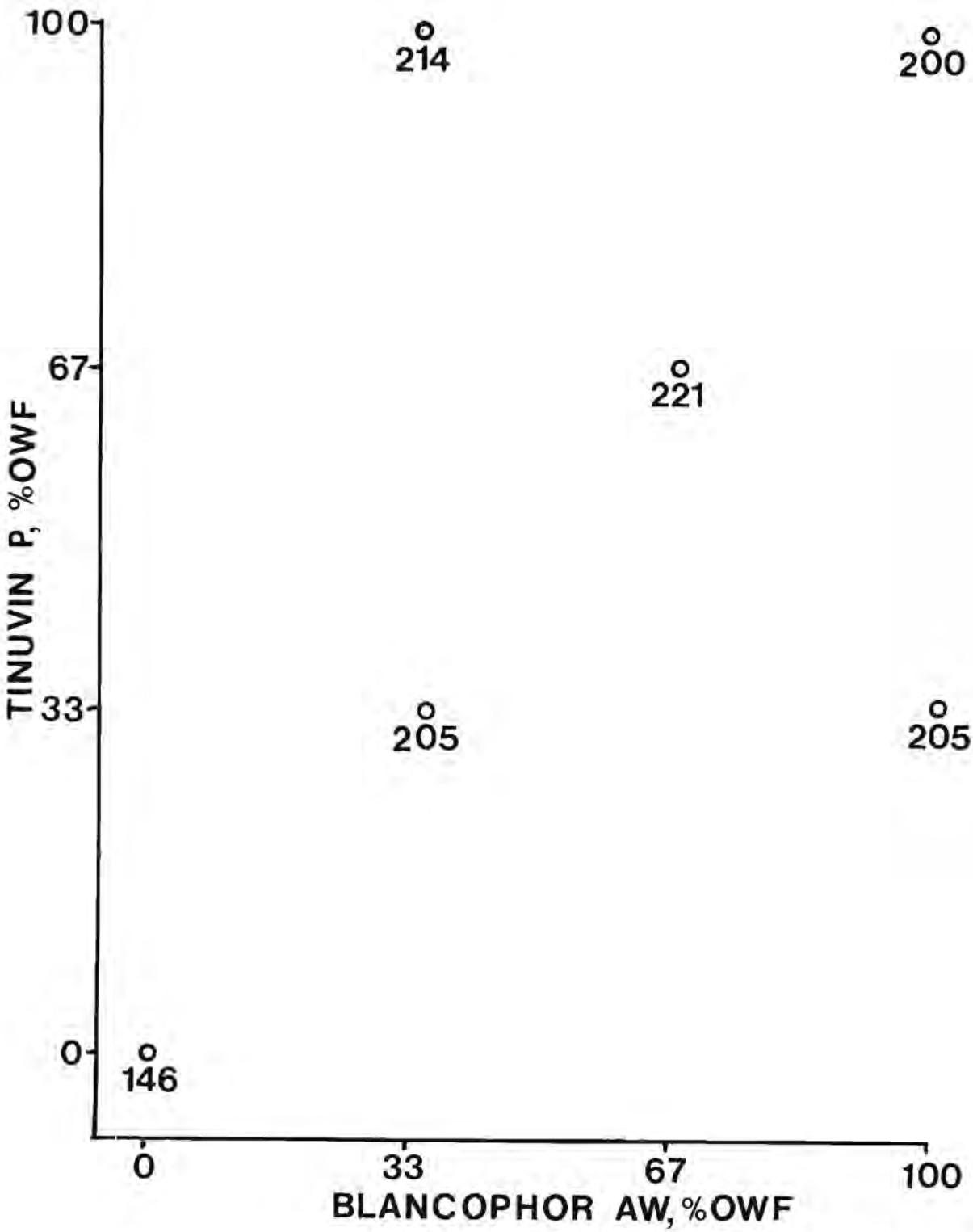

Figure 48. Strength after 100 hours exposure of Nomex fabric containing Blancophor AW and Tinuvin P.

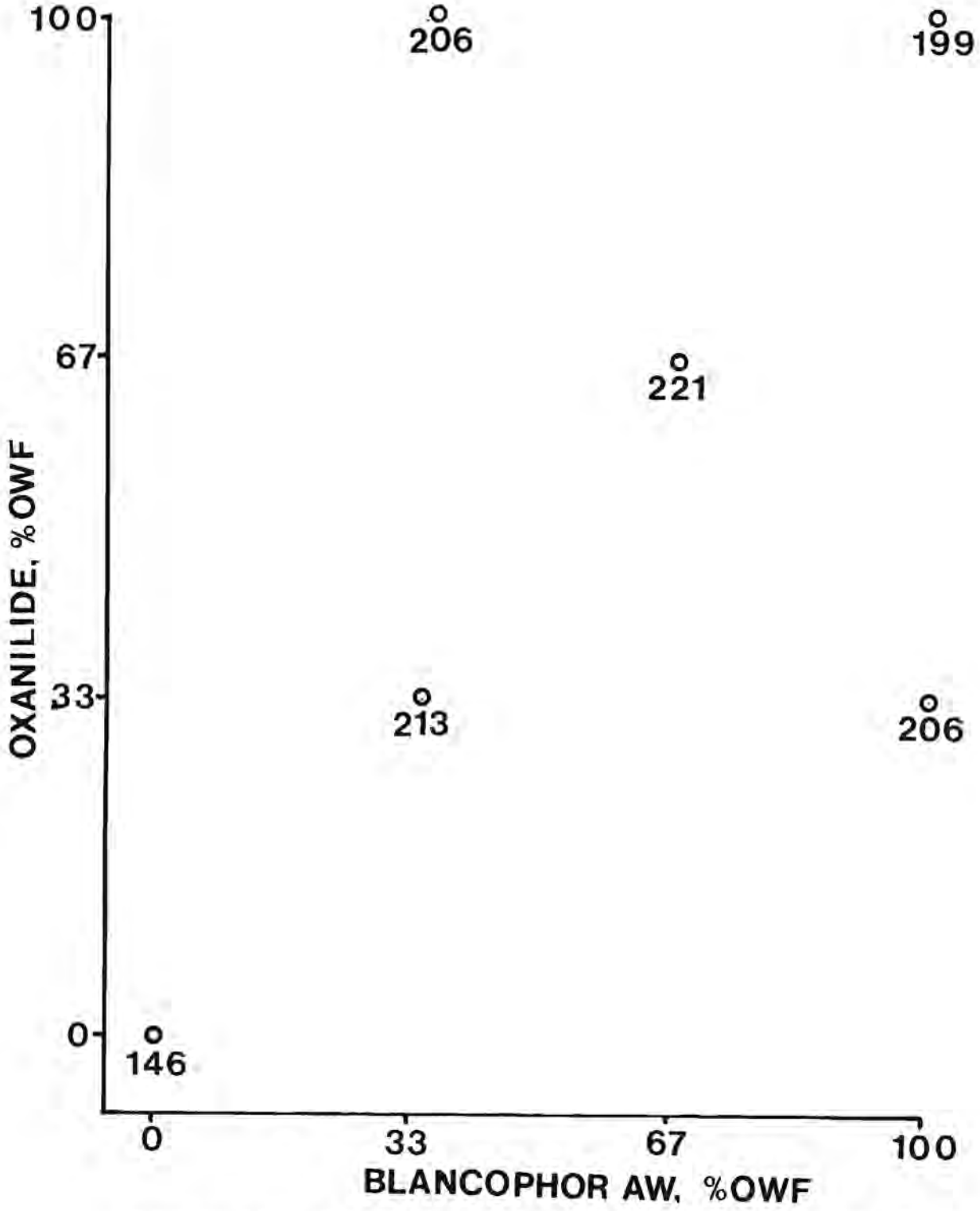

Figure 49. Strength after 100 hours exposure of Nomex fabrics containing oxanilide and Blancophor AW.

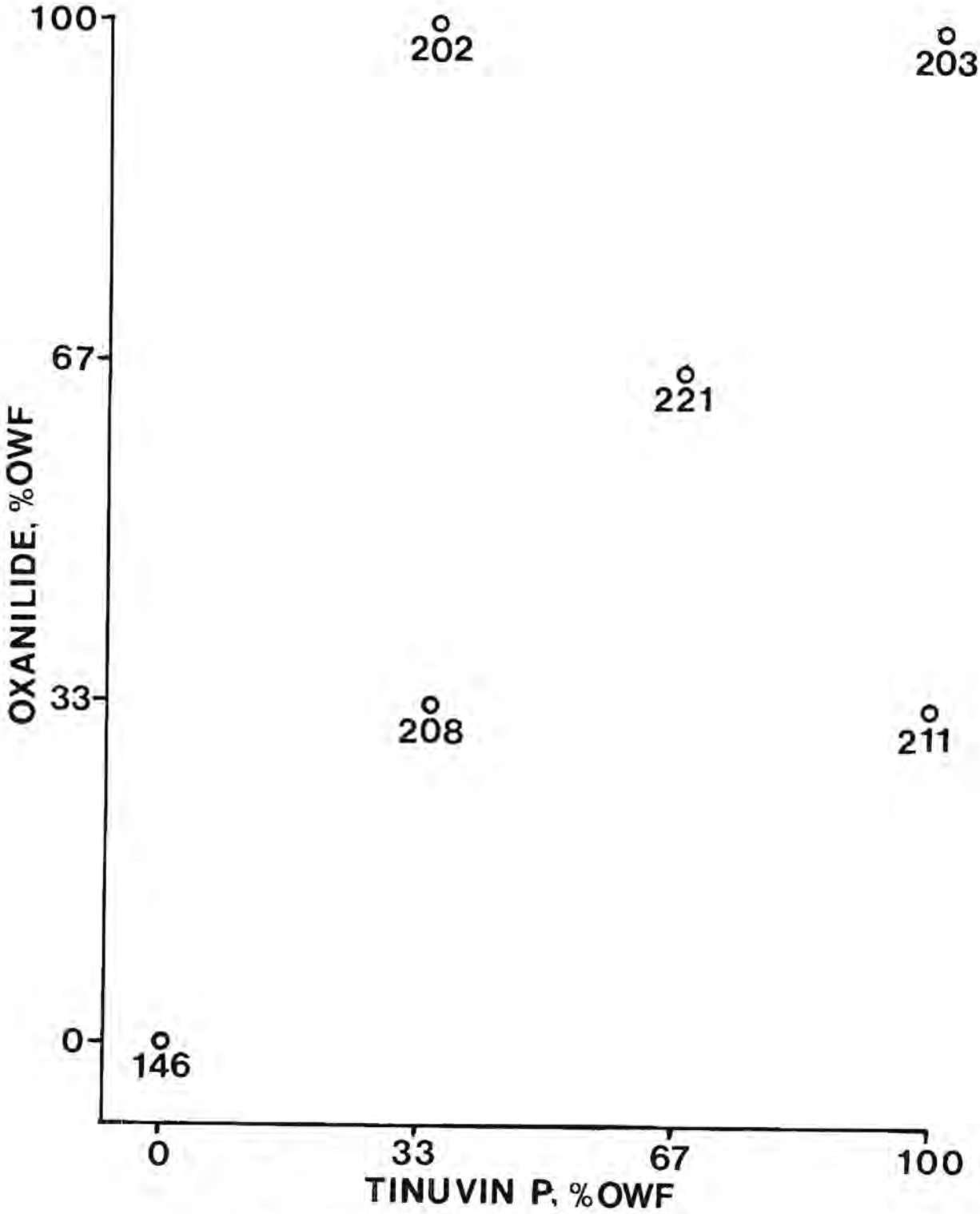

Figure 50. Strength after 100 hours exposure of Nomex fabrics containing oxanilide and Tinuvin P.

systems were selected which do not contain Blancophor AW to avoid the reduced dye lightfastness previously mentioned. Third, combinations were selected in which the level of Tinuvin P were usually higher than the other stabilizers. One of the selected systems was similar to the factorial sample which gave exceptionally high strength values both initially and after exposure.

The four systems selected for study were:

1. Blancophor AW 33%, Tinuvin P 33%, Oxanilide 33%
2. Blancophor AW 15%, Tinuvin P 50%, Oxanilide 15%
3. Tinuvin P 50%, Oxanilide 33%
4. Tinuvin P 50%

B. Evaluation of Stabilizer Systems

Nomex sage green fabric (Mil-C-38351,Type II,Class 1) obtained from Stern and Stern Textiles, Inc. was used in preparation of these samples. Pieces 10 inches by 15 yards (approximately 700 grams) were cut from the fabric and treated in a sample size Smith Engineering pressure jig dyeing machine. The fabric was attached to one of the jig rollers with surgical tape and the controller set to automatically cycle the fabric back and forth through the bath. The bath was filled with 29 liters of water and heated to the boil by means of an enclosed steam coil. Additives for a given run were weighed into a large beaker and mixed with 500 ml of the dyeing assistant, Chemocarrier FPN. The well dispersed additives were then added to the hot dyebath by pouring 1/4 of the mixture alternately in the two sides of the bath during one complete cycle of the jig. The jig was then closed and the pressure raised to 21-23 pounds per square inch (260°F) by injecting live steam into the bath. The fabric was cycled through the bath for 2 hours.

At the conclusion of the treatment cycle the fabric was washed at least 3 times in a standard washer and tumble dried to remove excess dyeing assistant and treatment chemicals.

A "blank-dyed" sample was also prepared which was subjected to the same treatment procedure as the treated samples except that no stabilizers were added to the bath. The sample identification numbers for the treated and control samples are given below:

Sample Number	Treatment
109-68-D	Control
109-68-A	Blank-dyed
109-68-E	33% Blancophor AW, 33% Tinuvin P, 33% Oxanilide
109-68-F	15% Blancophor AW, 50% Tinuvin P, 15% Oxanilide
109-68-C	50% Tinuvin P, 33% Oxanilide
109-68-B	50% Tinuvin P

In addition to tests in the Georgia Institute of Technology Laboratories, portions of each of the above samples were submitted to the Air Force Materials Laboratory for evaluation.

All samples were exposed to the carbon arc Fade-O-meter for periods of 50,100,150, and 200 hours. Before and after exposure the breaking load and elongation were determined by the 1" ravel strip method with the Instron tensile tester. Results are shown in Tables 4,5 and 6. The results are plotted in Figures 51 through 55 where the percent retention of breaking strength and elongation is plotted for each sample compared to the blank-dyed sample (109-68-A).

These data suggest that samples 109-68-E and 109-68-F showed greater resistance to UV degradation than the control or blank-dyed samples. Sample 109-68-E had 75% retention of breaking strength after 150 hours exposure which was the target objective for this project. Samples 109-68-B and 109-68-C showed less improvement than 109-68-E 109-68-F. This was undoubtedly due to the presence of Blancophor AW in both samples E and F. Sample E showed by far the best performance of any of the samples in strength retention.

An evaluation of the effects of treatment to increase UV stability on other fabric properties was also carried out for the six fabrics. The properties measured and the methods employed are given below.

TABLE 4

BREAKING STRENGTH AND ELONGATION BEFORE AND AFTER UV EXPOSURE

		Hours Exposed				
		0	50	100	150	200
109-68-D	Breaking Load	241.6	161.2	126.2	158.4	132.8
	Elongation	54.0	23.1	16.7	21.5	18.9
109-68-A	Breaking Load	241.3	182.0	131.4	125.2	122.4
	Elongation	54.2	26.2	19.2	23.0	21.8
109-68-E	Breaking Load	247.4	193.0	180.2	186.0	199.0
	Elongation	57.0	29.8	27.3	27.6	28.9
109-68-F	Breaking Load	253.6	196.6	146.0	132.8	149.0
	Elongation	63.2	28.4	27.5	27.2	32.6
109-68-C	Breaking Load	241.4	184.8	120.0	106.6	118.0
	Elongation	54.0	26.1	22.2	23.0	23.0
109-68-B	Breaking Load	218.8	145.2	125.4	130.2	126.6
	Elongation	49.9	25.2	27.2	25.7	25.6

TABLE 5

TENSILE STRENGTH RETENTION (%)

	Hrs. Exposed			
	50	100	150	200
109-68-D	66.7	52.2	65.6	55.0
109-68-A	75.4	54.5	51.9	50.7
109-68-E	78.0	72.8	75.2	80.4
109-68-F	77.5	57.6	52.4	58.8
109-68-C	76.5	49.7	44.2	48.9
109-68-B	66.4	57.3	59.5	57.9

TABLE 6

ELONGATION RETENTION (%)

	Hours Exposure			
Sample	50	100	150	200
109-68-D	43	31	40	35
109-68-A	48	35	43	40
109-68-E	52	48	48	51
109-68-F	45	44	43	52
109-68-C	48	41	43	43
109-68-B	51	55	51	58

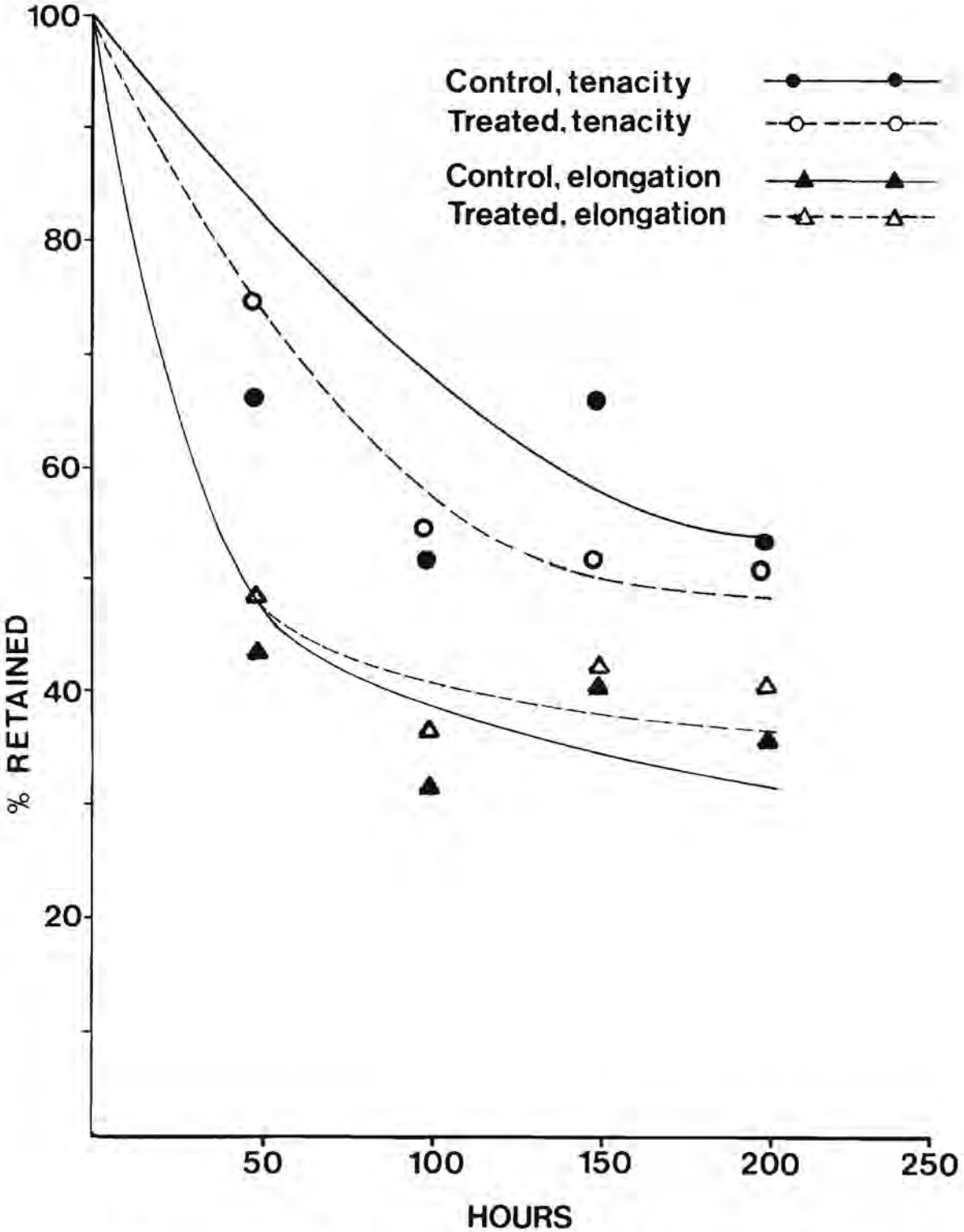

Figure 51. Retention of breaking strength and elongation of treated (a) and control (D) Nomex fabric after exposure in the carbon arc Fade-Ometer.

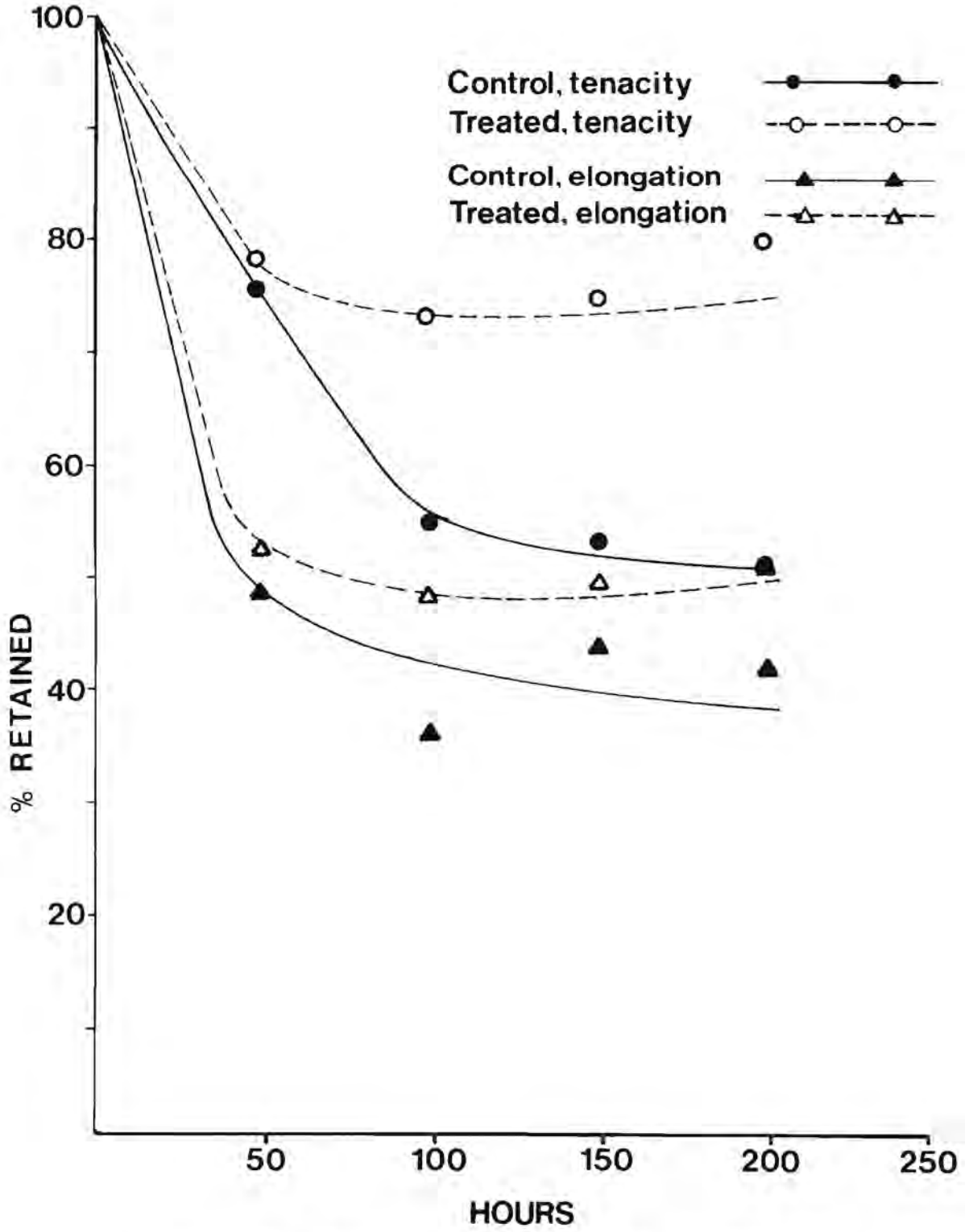

Figure 52. Retention of breaking strength and elongation of treated (E) and control (A) Nomex fabric after exposure in the carbon arc Fade-Ometer.

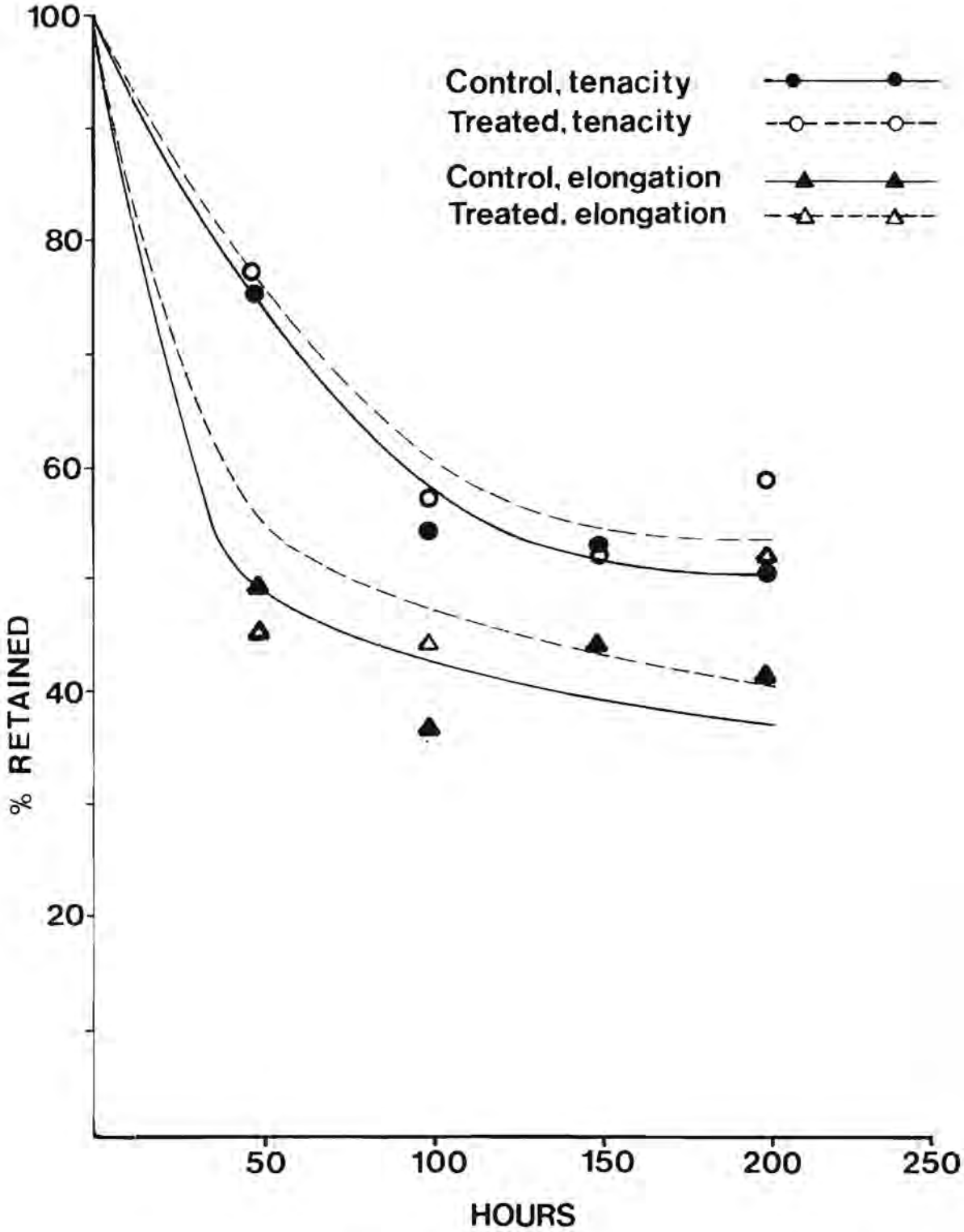

Figure 53. Retention of breaking strength and elongation of treated (F) and blank-dyed (A) Nomex fabric after exposure in the carbon arc Fade-Ometer.

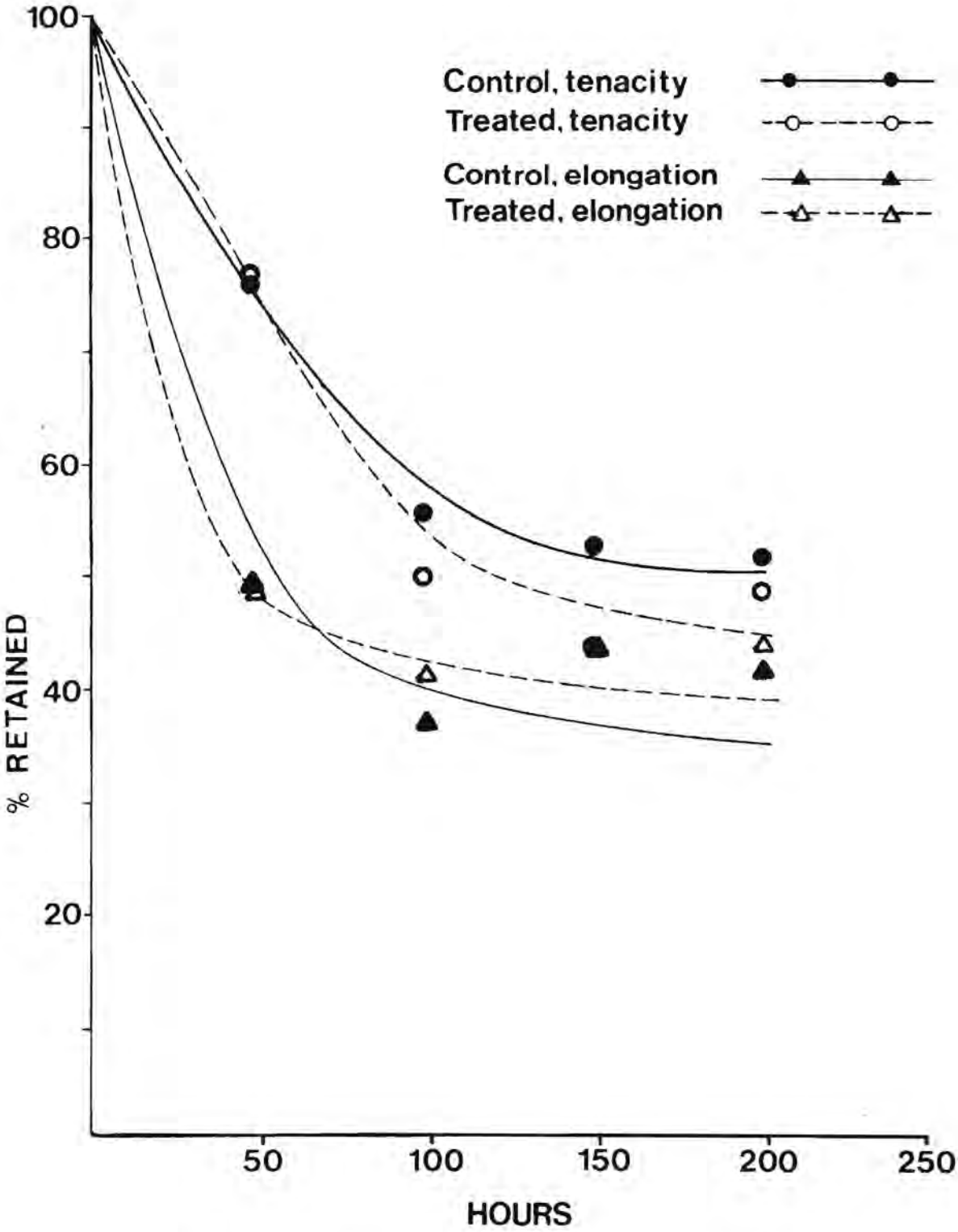

Figure 54. Retention of breaking strength and elongation of treated (C) and blank-dyed (A) Nomex fabric after exposure in the carbon arc Fade-Ometer.

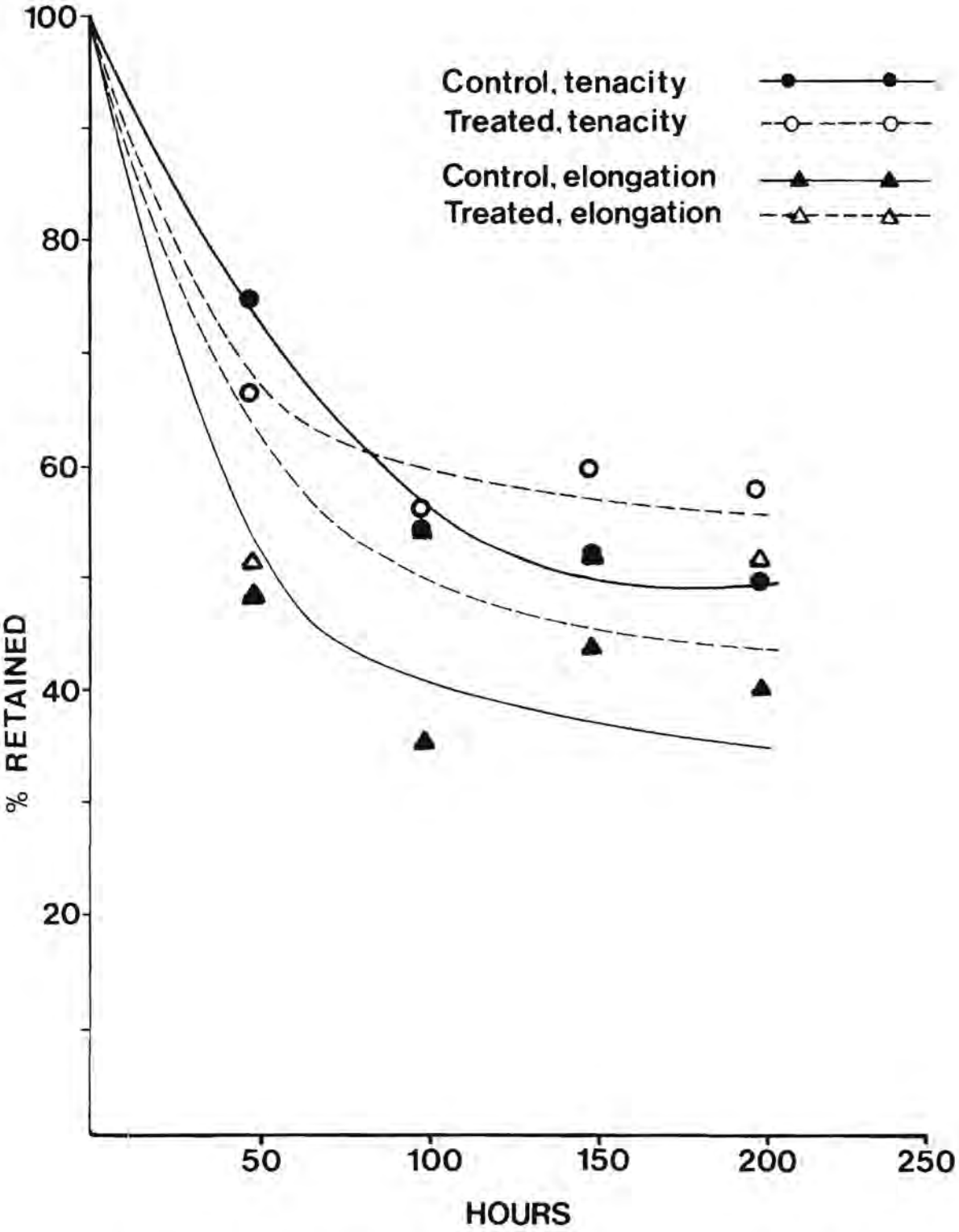

Figure 55. Retention of breaking strength and elongation of treated (B) and blank-dyed (A) Nomex fabric after exposure in the carbon arc Fade-Ometer.

Yarns per Inch

Warp ends per inch and filling picks per inch were measured as directed in Method 5050, Federal Test Method Standard 191. Results are shown in Table 7 and indicate that fabric construction was identical for all of the experiment fabrics.

Fabric Weight

Weight of the experimentally treated fabrics was measured according to Method 5041 of Federal Test Method Standard 191. Results are also shown in Table 7 and indicate a large difference in the measured weights among the samples, with the differences being related to the take-up of the UV stabilizer compounds by the fabric.

Thickness

Fabric thickness was measured according to Method 5030. Thickness varied among the several samples approximately the same as fabric weight and again is related to the take-up by the fabric of the UV resistant compound.

Flexibility

Flexibility was determined by measurement of bending length of the fabric in both the warp and filling directions. ASTM method D 1388, Stiffness of Fabrics, Option A-Cantilever Method, was used. Results indicate no consistency in bending length measurements among the several samples. Explanation of the differences observed will require a further examination.

Air Permeability

Air permeability was measured by the Frazier air permeability tester according to ASTM method D 737. The results indicate very high resistance to air passage through the fabric for all of the samples.

TABLE 7

PROPERTIES OF EXPERIMENTALLY-TREATED NOMEX FABRICS

Property	109-68-E	109-68-C	109-68-A	109-68-F	109-68-B	109-68-D
Warp Ends per Inch	63.2	62.8	62.0	62.6	63.0	62.2
Filling Picks per Inch	49.0	49.0	48.8	49.0	49.0	48.4
Weight, oz/sq.yd.	7.23	7.09	6.42	7.16	7.46	6.27
Thickness, inch	.012	.012	.010	.011	.011	.009
Flexibility: Bending Length,inches: Warp	4.77	4.10	3.53	4.56	4.40	3.23
Fill	7.07	3.44	3.55	5.70	3.82	4.20
Air Permeability, cu.ft./min.sq.ft.	3.2	2.6	1.7	1.9	2.2	2.4
Breaking Strength, lbs. Warp	247	241	241	254	219	242
Breaking Strength, lbs. Fill	189	176	177	185	186	170
Abrasion Resistance: Breaking Strength, lbs.; Warp	197	227	191	212	232	88
Breaking Strength, Retained	79	94	79	84	106	36
Breaking Strength, lbs.,Fill	179	189	145	190	179	64
Percent Strength Retained	95	107	82	103	96	38

Breaking Strength

Breaking strength was measured according to ASTM method D 1682, 1-inch ravelled strip test. Filling strength of all samples was approximately the same, while warp strength of sample B was lower than that of the other samples.

Abrasion Resistance

This property was measured following ASTM method D 1175, flexing and abrasion method. Specimens 1 1/2" x 10" were ravelled to a width of 1 inch and abraded for 900 cycles with a tension load of 4 pounds and a head load of 1 pound. Strength of the abraded specimens was measured according to ASTM method D 1682. Percent breaking strength retained is shown in Table 7 and indicates that all of the treatments, including the blank dyeing, improved the abrasion resistance.

Results of the warp ends and picks per inch indicate that little dimensional change occurred during the treatment. The weight measurements show a 13 to 19% increase in weight as a result of treatment. From the appearance of the fabric it is probable that at least part of this weight increase is due to chemicals on the fabric surface which were not completely removed by the after-scouring step. Fabric flexibility was decreased somewhat as a result of the treatment.

One result which was not expected was the increase in abrasion resistance observed for the treated fabrics and the blank-dyed fabric. It is apparent that the dyeing operation has a very beneficial effect on abrasion properties and may be due to either lubrication of the fabric by carrier components or to changes due to thermal treatment during the process.

Treated, control and blank-dyed samples were tested also in accordance with DOC-FF-3-71. Measurement of after-flame times, afterglow times and char lengths are given in Table 8. Afterglow times were comparable for all the samples tested and with the exception of sample 109-68-E, the char lengths were similar. Greater variation was observed in the afterflame times. Samples 109-68-E and 109-68-C appear to have higher afterflame times. Since samples 109-68-E and 109-68-C both have 33% Oxanilide,

TABLE 8

RESULTS OF VERTICAL FLAME TEST ON CONTROL, TREATED, AND BLANK-DYED FABRICS

Sample	Afterflame Time (sec.)	Afterglow Time (sec.)	Charlength
109-68-D warp	4.4	0.9	1.5
109-68-D filling	3.8	4.5	1.4
109-68-A warp	4:1	0.0	1.4
109-68-A filling	3.5	0.2	1.2
109-68-E warp	9.8	0.0	3.3
109-68-E filling	10.8	0.0	4.8
109-68-F warp	2.6	0.8	1.0
109-68-F filling	3.8	0.0	1.6
109-68-C warp	14.1	0.0	2.1
109-68-C filling	15.9	0.0	1.4
109-68-B warp	8.1	0.0	2.5
109-68-B filling	2.1	0.6	0.9

this component of the treatment system may have an adverse effect on flammability. Reduction in the level of oxanilide in the treatment selected for final recommendations was considered as this appears to be the least effective component in improving the UV stability of Nomex.

C. Improvement in Treating System

Some disadvantages of the treatment system were noted during preparation of the six samples described above. The dyeing assistant used was not properly emulsified for use in a low agitation system such as the pressure jig. Accumulation of solids during the treatment cycle made cleanup of the jig and the fabric at the end of the treatment a major problem.

A survey of dyeing systems that would be useful for Nomex treatment was conducted and a jet dyeing machine was evaluated for this purpose. The jet machine with high agitation of the dye liquor was expected to offer some advantages over the pressure jig.

Jet dyeing was investigated as a means of treating Nomex fabric. A sample of fabric 12 inches by 30 feet was treated in a mini-jet dyeing machine at the Celanese Laboratory in Charlotte, North Carolina. The treatment bath contained 33% Blancophor AW, 15% Tinuvin P and 7% Oxanilide. Results of testing of this sample (109-68-H) compared to the two best samples from dyeing (109-68-E and 109-68-F) are shown in Table 9. The 73% retention of tensile strength and 54% retention of elongation after 150 hours exposure to the carbon arc are remarkable good considering that the weight pick-up in jet dyeing was only 5.42% (compared to 15.3% for sample 109-68-E and 14.2% for 109-68-F). Jet dyeing was the treatment technique selected for preparation of large samples of Nomex fabric.

D. The Selected Treatment System

Data on strength retention for all treated fabric samples are summarized in Table 10. The quantity of each of the additives (in percent owf) in the treatment bath are shown in parenthesis for Blancophor AW, Tinuvin P, and Oxanilide, respectively. The xenon and carbon arc exposures were conducted at the Georgia Tech laboratories, the sunshine arc exposures at U.S. Testing Laboratories and the outdoor exposures at the South Florida Testing Service.

TABLE 9

COMPARISON OF NOMEX SAMPLES TREATED IN A JET AND JIG DYEING MACHINE

Tensile Strength

Sample	0 hrs	50 hrs	100 hrs	150 hrs	200 hrs
109-68-E	247	193	180	186	199
109-68-F	254	197	146	133	149
109-68-H	229	167	157	167	161

Elongation

Sample	0 hrs	50 hrs	100 hrs	150 hrs	200 hrs
109-68-E	57	30	27	28	29
109-68-F	63	28	28	27	33
109-68-H	63	37	34	34	31

TABLE 10

STRENGTH RETENTION (%) OF TREATED NOMEX FABRICS AFTER EXPOSURE

Carbon Arc Exposure

Sample	% Tensile Strength Retention 50 hr	100 hr	150 hr	200 hr
109-68-E (33,33,33)	78	73	75	80
109-68-F (15,50,15)	76	58	52	59
109-68-C (0,50,33)	77	50	44	49
109-68-B (0,50,0)	66	57	60	58
109-68-D (0,0,0)	67	52	66	55

Sunshine Arc Exposure

Sample	% Tensile Strength Retention 50 hr	100 hr	150 hr	200 hr
109-68-E (33,33,33)	72	77	70	55
109-68-F (15,50,15)	69	63	63	54
109-68-C (0,50,33)	65	62	55	53
109-68-B (0,50,0)	70	67	62	60
109-68-D (0,0,0)	63	64	53	48

Xenon Arc Exposure

Sample	% Tensile Strength Retention 50 hr	100 hr	150 hr	200 hr
109-68-E (33,33,33)	90	86	82	80
109-68-F (15,50,15)	89	82	79	73
109-68-C (0,50,33)	79	70	66	61
109-68-B (0,50,0)	87	74	72	67
109-68-D (0,0,0)	77	73	67	67

Florida Sunshine

Sample	% Tensile Strength Retention 1 month	2 months	3 months
109-68-E (33,33,33)	73	50	50
109-68-F (15,50,15)	69	52	47
109-68-C (0,50,33)	68	53	47
109-68-B (0,50,0)	72	60	55
109-68-D (0,0,0)	69	53	49

It is apparant from these data that, with the exception of the South Florida exposures, those fabrics with all three additives (Samples 109-68-E and 109-68-F) performed best. In the South Florida exposures Sample 109-68-B containing only Tinuvin P was comparable to 109-68-E. It was decided that the treatment system used for large fabric samples should contain both Blancophor AW and Tinuvin P at 33% (owf) in the treatment bath. It was decided that oxanilide, although apparantly effective in the three component systems, was more effective at lower concentrations. Also, flammability studies reported earlier suggested that oxanilide at high levels may increase the flammability as measured by the vertical flame test. Therefore, an oxanilide level of 50% (owf) was selected for the large fabric and webbing samples.

SECTION IV

PREPARATION AND EVALUATION OF FABRIC AND WEBBING SAMPLES

A. Preparation of Fabric Sample

Final evaluation of the selected stabilizer system was carried out by treating 200 yards of Nomex sage green fabric (Mil-C-38-351,Type II,Class I) and 100 yards of Nomex sage green webbing (Mil-W-38283,Type XII). The fabric was obtained from Stern and Stern Textiles and the webbing was produced by Murdock Webbing Company.

The fabric sample was treated in a Gaston County 100# Jet Dyeing Machine at the Monsanto Textile Company laboratories in Decatur, Alabama.

The dyeing machine was filled with 350 gallons of water, the fabric (109 pounds) was entered and wet-out by passing through the jet at 150 yards per minute. The temperature was raised to 120°F at 3°F per minute prior to addition of the treatment chemicals. A treatment solution concentrate was prepared by dispersing

36 pounds	Blancophor AW	(33% owf)
36 pounds	Tinuvin P	(33% owf)
5.5 pounds	Oxanilide	(5% owf)

in 17.5 gallons of Chemocarrier FPN (Tanatex). The Blancophor AW and Oxanilide were soluble in the carrier but the Tinuvin P is not soluble at room temperature. The treatment solution was placed in the add tank, heated with steam to approximately 120°F and added to the jet machine by circulating part of the bath through the add tank. After complete addition of the stabilizer the temperature was raised to 270°F at 3° F per minute and held at 270°F for 2 hours. The bath was cooled to 160°F at 3°F per minute and overflow rinsed for 10 minutes (about 2 bath volumes). The bath was then discharged and the dyeing machine refilled with water and heated to 160°F. A scouring agent, Merpol LFH (1%), was added and the fabric run for 10 minutes followed by 10 minutes of overflow rinsing. The bath was then dumped and the scouring step repeated twice. Following the scouring, the sample was overflow rinsed for 10 minutes, unloaded, vacuum extracted to remove excess water and dryed (33 seconds at 250°F followed by 33 seconds at 300°F).

B. Preparation of Webbing Sample

Approximately 100 yards of Nomex webbing (Mil-W-38283,Type XII) were given the selected treatment to improve resistance to UV degradation. The webbing was woven by Murdock Webbing Company, Inc. and treated in a Gaston County Sample Jet Dyeing Mahine, Model PBJ-1100, at Hoechst Fibers laboratories in Greenville, South Carolina. The webbing was loaded in the jet machine (25 pounds) and the machine filled with 125 gallons of water at 120°F. The temperature was raised to 190°F at approximately 3°F per minute. The treatment solution containing 8.25 pounds of Blancophor AW, 8.25 pounds of Tinuvin P, and 1.25 pounds of oxanilide dispersed in 6.25 gallons of Chemocarrier FPN was added through the expansion tank at 190°F. The treatment bath was heated to 265°F at 3°F per minute and held at that temperature for 2 hours. Following the treatment, the bath was lowered to 190°F and dropped. The sample was then hot rinsed at 170°F for 5 minutes and overflow rinsed at 160°F for 15 minutes. The webbing was scoured at 160°F for 5 minutes in 2% (owf) Merpol LFH followed by a 5 minute overflow rinse at 160°F. The sample was then given a cold running rinse for 20 minutes squeezed dry in a pad and dried at 300°F in a 20 foot dryer at 2 yards per minute. The treated webbing was returned to Murdock Webbing Company for resin treatment as specified for Mil-W-38283,Type XII.

C. Evaluation of Treated Fabric

Specimens of treated and untreated fabric were exposed for periods of 50,100,150 and 200 hours to the xenon arc, carbon arc, and Sunshine arc lamps. Breaking load and elongation were determined in the warp and filling direction after each exposure period by the 1" ravel strip method described previously. Breaking strength and elongation before and after exposure to xenon, carbon and Sunshine arc lamps are given in Tables 11,12 and 13; the retention of breaking strength (in percent) in Tables 14, 15 and 16; and the retention of elongation (in percent) in Tables 17,18, and 19.

It is apparent from these data that the treatment system resulted in significant improvement in the UV resistance of the Nomex fabric. Tensile strength for the treated fabric after 150 hours exposure to the Sunshine arc was 89% in the warp direction and 87% in the filling direction compared to 49% and 46% for the untreated fabric. Similar results (83 and 78% versus 58 and 53%)

TABLE 11

BREAKING STRENGTH AND ELONGATION OF UNTREATED AND TREATED NOMEX SPECIMENS BEFORE AND AFTER EXPOSURE TO SUNSHINE ARC LIGHT.

Material and Pull Direction	Hours Exposed				
	0	50	100	150	200
Untreated					
Warp - Breaking Load	249.2	166.6	137.8	123.0	104.6
Elongation (%)	47.8	21.3	16.9	15.9	18.9
Filling - Breaking Load	199.0	123.6	91.8	91.8	59.2
Elongation (%)	39.9	12.1	7.2	6.7	6.1
Treated					
Warp - Breaking Load	247.8	220.6	222.2	220.8	208.2
Elongation (%)	54.5	41.3	42.0	40.3	38.9
Filling - Breaking Load	209.4	178.2	185.0	181.8	179.2
Elongation (%)	43.6	23.7	24.4	24.3	24.6

TABLE 12

BREAKING STRENGTH AND ELONGATION OF UNTREATED AND TREATED NOMEX SPECIMENS BEFORE AND AFTER EXPOSURE TO XENON ARC LIGHT.

Material and Pull Direction		Hours Exposed				
		0	50	100	150	200
Untreated						
Warp -	Breaking Load	249.2	179.2	159.4	144.0	134.6
	Elongation (%)	47.8	24.6	20.8	18.2	16.5
Filling -	Breaking Load	199.0	148.6	125.6	105.2	90.4
	Elongation (%)	39.9	14.9	9.7	7.8	7.0
Treated						
Warp -	Breaking Load	247.8	226.4	212.4	204.6	208.6
	Elongation (%)	54.5	41.3	37.2	34.0	35.1
Filling -	Breaking Load	209.4	180.4	171.6	163.8	167.0
	Elongation (%)	43.6	25.3	21.6	19.0	20.8

TABLE 13

BREAKING STRENGTH AND ELONGATION OF UNTREATED AND TREATED NOMEX SPECIMENS BEFORE AND AFTER EXPOSURE TO CARBON ARC LIGHT.

Material and Pull Direction		Hours Exposed				
		0	50	100	150	200
Untreated						
Warp -	Breaking Load	249.2	170.2	134.2	122.0	106.4
	Elongation (%)	47.8	22.5	18.7	22.6	20.4
Filling -	Breaking Load	199.0	125.6	97.0	79.0	63.8
	Elongation (%)	39.9	11.9	7.0	7.3	6.7
Treated						
Warp -	Breaking Load	247.8	212.4	180.0	133.2	130.0
	Elongation	54.5	36.6	29.5	27.1	25.9
Filling -	Breaking Load	209.4	174.4	135.2	101.8	96.4
	Elongation (%)	43.6	21.5	15.3	11.0	8.9

TABLE 14

TENSILE STRENGTH RELATION (%)
(SUNSHINE ARC LIGHT)

Sample	Duration of Exposure in Hours			
	50	100	150	200
Untreated Nomex				
Warp	66.9	55.3	49.4	42.0
Filling	62.1	46.1	46.1	29.7
Treated Nomex				
Warp	89.0	89.7	89.1	84.0
Filling	85.1	88.3	86.8	85.6

TABLE 15

TENSILE STRENGTH RETENTION (%)
(XENON ARC LIGHT)

Sample	Duration of Exposure in Hours			
	50	100	150	200
Untreated Nomex				
Warp	71.9	64.0	57.8	54.0
Filling	74.7	63.1	52.9	45.4
Treated Nomex				
Warp	91.4	85.7	82.6	84.2
Filling	86.2	81.9	78.2	79.8

TABLE 16

TENSILE STRENGTH RETENTION (%)
(CARBON ARC LIGHT)

Sample	Duration of Exposure in Hours			
	50	100	150	200
Untreated Nomex				
Warp	68.3	53.9	49.0	42.7
Filling	63.1	48.7	39.7	32.1
Treated Nomex				
Warp	85.7	72.6	53.8	52.5
Filling	83.3	64.6	48.6	46.0

TABLE 17

ELONGATION RETENTION (%)
(SUNSHINE ARC LIGHT)

Sample	Duration of Exposure in Hours			
	50	100	150	200
Untreated Nomex				
Warp	44.6	35.4	33.3	39.5
Filling	30.3	17.6	16.8	15.3
Treated Nomex				
Warp	75.8	77.1	73.9	71.4
Filling	54.4	56.0	55.7	56.4

TABLE 18

ELONGATION RETENTION (%)

(XENON ARC LIGHT)

Sample	Duration of Exposure in Hours			
	50	100	150	200
Untreated Nomex				
Warp	51.5	43.5	38.1	34.5
Filling	37.3	24.3	19.5	17.5
Treated Nomex				
Warp	75.8	68.3	62.4	64.4
Filling	58.0	49.5	43.6	47.7

TABLE 19

ELONGATION RETENTION (%)

(CARBON ARC LIGHT)

Sample	Duration of Exposure in Hours			
	50	100	150	200
Untreated Nomex				
Warp	47.1	39.1	47.3	42.7
Filling	29.8	17.5	18.3	16.8
Treated Nomex				
Warp	67.2	54.1	49.7	47.5
Filling	49.3	35.1	25.2	20.4

were obtained for xenon arc exposure. The carbon arc appears to be a much more severe exposure source as the treated fabric retains 54 and 49% of the tensile strength in the warp and filling direction and the untreated sample only 49 and 40%. Retention of elongation after exposure of treated and untreated samples shows trends that are very similar to the tensile strength retention data.

D. Evaluation of Webbing Samples

The breaking strength of webbing samples was determined in accordance with FED-STD-191-4108 except that only 3 specimens were tested for each condition. This modification was made due to the very large quantity of material required for each test. Data on breaking strength of webbing (treated and untreated) before and after 150 hours exposure to the Sunshine arc are given in Table 20. There is little loss in breaking strength due to exposure of the webbing to UV light. This is undoubtedly due to the thickness of the webbing. Most of the fibers are not exposed to the UV light in this type structure. The control fabric retained 93% of the original strength and the treated fabric was essentially undegraded by the exposures. More extensive exposures were not undertaken, again, due to the large quantity of webbing required for breaking strength tests.

TABLE 20

TENSILE STRENGTH OF NOMEX WEBBING
BEFORE AND AFTER SUNSHINE ARC EXPOSURE

	Tensile Strength (pounds)	
Untreated	0 hours exposure	150 hours exposure
	6300	5860
	6260	5860
	6240	5840
	AV 6267	AV 5853
Treated	5660	5640
	5720	5720
	5660	5660
	AV 5680	AV 5673

SECTION V

CONCLUSIONS

The objective of this project was the development of a treatment system for Nomex fabric which would yield 75% retention of the tensile strength after 150 hours exposure to the Atlas Sunshine Carbon Arc Fade-Ometer. This objective was achieved by treatment of fabric samples with a solution containing 33% (owf) Blancophor AW, 33% (owf) Tinuvin P, and 5% (owf) Oxanilide using Chemocarrier FPN as a carrier in a modified jet dyeing procedure. Retention of tensile strength of treated samples was 89% in the warp direction and 87% in the filling direction after exposure for 150 hours to the sunshine arc lamp. Untreated fabrics show less than 50% retention of tensile strength under similar exposure conditions.

Most typical UV stabilizers have little effect on the stability of Nomex to UV exposures. Seventy five materials were screened for effectiveness in stabilizing Nomex but only Blancophor AW, Oxanilide, and Tinuvin P improved the light stability.

SECTION VI

RECOMMENDATIONS

Attempts should be made to optimize the stabilizer system to achieve more economical treatment. It may be possible to reduce the quantity of stabilizers used significantly with little or no reduction in UV stability.

A "standing bath" solvent treatment technique would probably be preferred to the modified drying procedure used in the present work. Such a system could substantially reduce the cost of treating Nomex to improve UV stability.

More extensive outdoor exposure studies should be conducted on treated Nomex samples for comparison with the data obtained by carbon arc and xenon arc exposure.

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APPENDIX A

LITERATURE SURVEY

The computer search of Chemical Abstracts from July, 1968, to Dec. 1975, has been completed using the list of descriptors shown in Table 1. The computer listed over 1,000 citations of which 188 were selected for inclusion in the bibliography shown in the Appendix. Many references to new aromatic amide compositions showing improved thermal stability and references to the more prosaic and standard stabilizers for thermal degradation of aliphatic amides were not included in the list as these subjects are less pertinent to the present work. The selected references have been divided into 12 categories.

A. General Papers on UV Degradation
B. UV Degradation of Nylon 6 and Nylon 6,6
C. Thermal Degradation of Nylon 6 and Nylon 6,6
D. Thermal Stabilizers for Nylon 6 and Nylon 6,6
E. UV Stabilizers for Nylon 6 and Nylon 6,6
F. Thermal Degradation of Aramids
G. UV Degradation of Aramids
H. Thermal Stabilizers for Aramids
I. UV Stabilizers for Aramids
J. Dyeing of Aramids
K. Stability and Degradation of Phenolic Fibers
L. Photochemistry of the Amide Bond

In the important area of UV stabilizers for Aramids 13 references were discovered. Many of the stabilizers reported are not practical systems for use on Nomex fabric. The literature, therefore, provided little guidance in selection of compounds for Nomex stabilization.

Twelve references have been found that discuss the mechanism of radiation and UV degradation of Nomex and other aramids. These references were useful in selection of some materials for screening studies.

TABLE 1.

DISCRIPTOR LIST NOMEX DEGRADATION SEARCH

Group	Term No.	Term	Group	Term No.	Term
G001	1	Nomex	G002	23	*Phenyl*
G001	2	Aramid	G002	24	*Phthal*
G001	3	Poly(1,3-Phenylene Isophthalamide)	G002	25	*Tolyl*
G001	4	Poly(1,4-Phenylene Terephthalamide)	G002	26	*Pryidyl*
G001	5	Poly(1,3-Phenylene Terephthalamide)	G002	27	*Naphythyl*
G001	6	Poly(1,4-Phenylene Isophthalamide)	G002	28	*Aryl*
G001	7	Poly(4-Aminobenzoic Acid)	G002	29	*Anthryl*
G001	8	Poly(3-Aminobenzoic Acid)	G002	30	Arene*
G001	9	Kevlar	G003	31	Poly*
G001	10	Fiber B	G003	32	Macromol*
G001	11	HT-1	G003	33	Macromol*
G001	12	HT-4	G004	34	*Amide*
G001	13	PRD 49	G005	35	UV
G002	14	Aromatic*	G005	36	U.V.
G002	15	Arom	G005	37	U. V.
G002	16	*Benz*	G005	38	Ultraviolet
G002	17	*Isoquino*	G005	39	Ultra-violet
G002	18	*Indol*	G005	40	Light
G002	19	*Iden*	G005	41	Decompos*
G002	20	*Indazol*	G005	42	Decompn
G002	21	*Indanyl*	G005	43	Degrad*
G002	22	"Fluoren*	G005	44	Degrdn

TABLE 1. (cont'd.)

DISCRIPTOR LIST NOMEX DEGRADATION SEARCH

Group	Term No.	Term	Group	Term No.	Term
G005	45	Breakdown*	G006	61	Thermal
G005	46	Break-down*	G006	62	*Flam*
G005	47	Breaking Down*	G006	63	Fire*
G005	48	Unzip*	G007	64	Resist*
G005	49	Cleav*	G007	65	*Proof*
G005	50	*Stabi*	G007	66	*Retard*
G005	51	*Stable*	G008	67	Nylon*
G005	52	Deteriorat*	G009	68	High Temp*
G005	53	Degenerat*	G009	69	Nonflammable
G005	54	Reaction	G009	70	Non-flammable
G005	55	Depolymeriz*	G010	71	Kynol
G005	56	Depolymn	G010	72	Polybenzimidazole
G005	57	Hydroly*	G010	73	Poly(Benzimidazole)
G005	58	Solvoly*	G010	74	PBI
G005	59	Photoly*	G010	75	P.B.I.
G006	60	Heat	G010	76	P. B. I.

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APPENDIX B

STABILIZERS FOR E-11 NOMEX FABRIC

Samples of the experimental E-11 (which is considered for replacement of Nomex in stable yarn applications) Nomex fabrics have been treated in "dyebaths" containing Tinuvin P and Blancophor AW. The treated fabrics have been exposed for 20 and 60 hours in the carbon-arc fadeometer and the elongation and breaking strength determined in the warp direction by the 1" ravel strip method. Results are shown in Figures B-1 and B-2 where percent retention of breaking strength and elongation are compared for treated and blank dyed samples. These results clearly indicate that systems which stabilize regular Nomex are also effective on E-11 fabrics. The results are consistent with the proposed structure of E-11 yarn (a fiber blend of predominantly regular Nomex with a small quantity of a more thermally stable fiber).

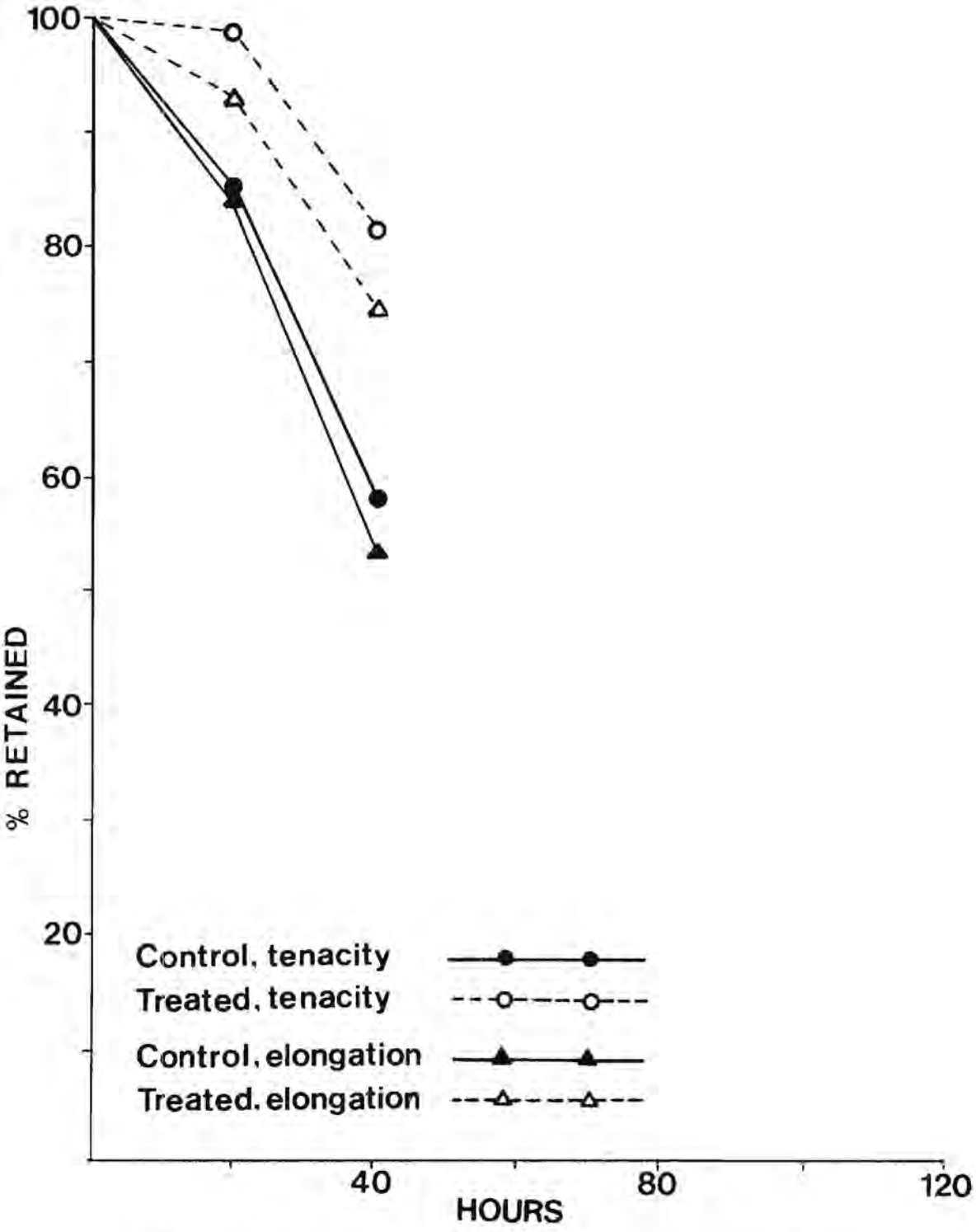


Figure B1. Retention of elongation and breaking strength for E-11 Nomex fabric containing Blancophor AW compared to blank dyed fabric.

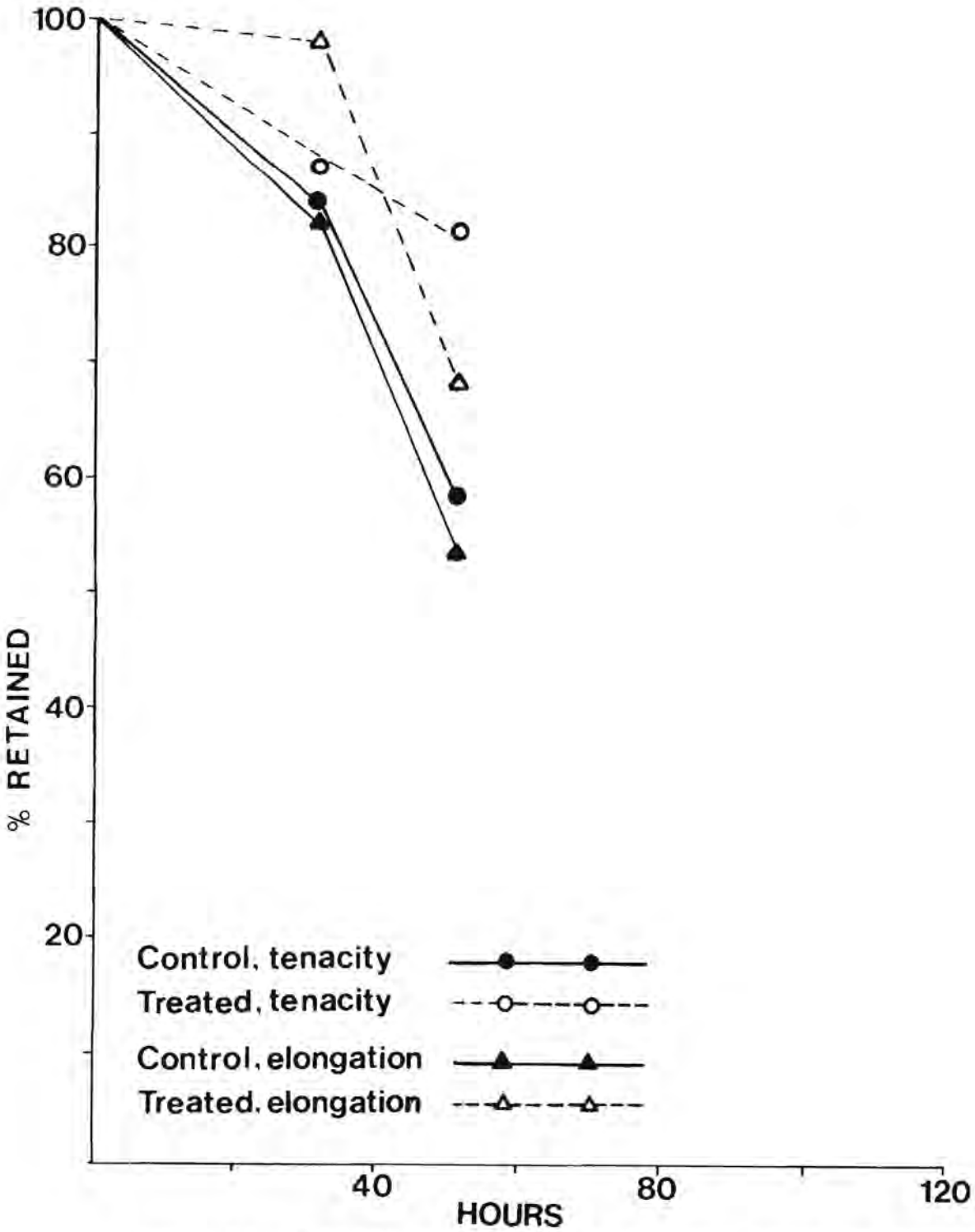
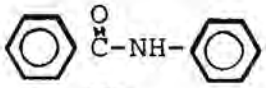


Figure B2. Retention of elongation and breaking strength for E-11 Nomex fabric containing Tinuvin P compared to control sample.

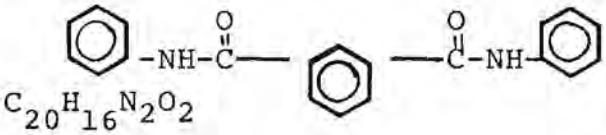
APPENDIX C

FUNDAMENTAL STUDIES ON NOMEX UV DEGRADATION

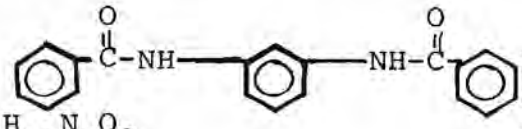
In order to evaluate the mechanistic characteristics of the UV degradation of Nomex, three model compounds were chosen for study in solid state photolysis experiments. These model Compounds were:

1)  Benzanilide

$C_{13}H_{11}NO$

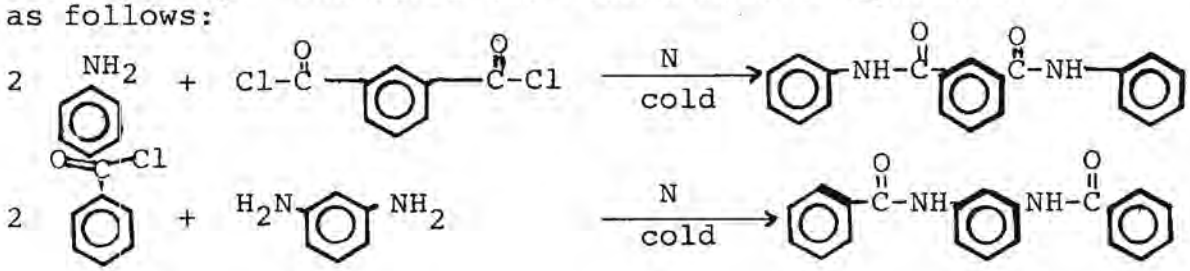
2)  Isophalanilide or N,N'-diphenyl-1-3-benzene-dicarboxamide

$C_{20}H_{16}N_2O_2$

3)  N,N'-dibenzoyl-m-phenylene-diamine or N,N'-m-phenylenebis-benzamine

$C_{20}H_{16}N_2O_2$

Benzanilide was purchased from Aldrich Chemical Company at 99.9% purity. The other two models must be synthesized as follows:



The analytical data, i.e., IR, NMR, mass spectra, and melting point shown are consistent with the expected products. The thermal stability of these materials was studied by DTA/TGA in air and N_2 and compared with Nomex as shown in Table C-1.

TABLE C-1. THERMAL PROPERTIES OF NOMEX AND MODEL STRUCTURES

	wt. (mg)	Atmos.	Peak temp.	% wt. loss at peak	type peak	
	18.39	air	163°C	0	endo	mp
			325°C	76	endo	subline
			372°C	24	exo	
	27.02	N_2	164°C	0	endo	mp
			360°C	100	endo	sublime
	13.16	air	289°C	0	endo	mp
			410°C	37	exo	
	12.10	N_2	490°C	45	exo	
			633°C	18	exo	
	10.30	air	236°C	0	endo	mp
			455°C	69	exo	
			660°C	31	exo	
	13.62	N_2	235°C	0	endo	mp
			377°C	31	endo	
			478°C	18	exo	
			640°C	31	exo	
Nomex	15.30	air	312°C	4	endo	
			620°C	96	exo	
			765°C	96	exo	
	15.27	N_2	380°C	5	exo	
			542°C	95	exo	
			900°C	95	endo	

The data from the DTA/TGA system were plotted as % weight loss vs. temperature. A series of four pairs of curves were obtained and the curves are of the same general shape. The nigrogen and air curves fall on top of one another. This is indicative that the materials undergo similar thermal degradation. As a matter of interest, it should be noted that Nomex in air and N_2 has the exact opposite type of DTA peak initially. In air, there is an endotherm characteristic of bond breaking and in N_2 there is an exotherm characteristic of bond formation. It is felt the exotherm is some cyclization process occuring, and this may be masking the endotherm or the endotherm may not be present at all.

Each model compound was dissolved in DMF and a 1 ml. aliquots from standard solutions were evaporated on a 3" by 1" glass slide. This procedure left behind 10 mg. of material. These samples were then mounted and exposed to UV light from a 2500 watt Xenon arc lamp source at a relative humidity of 52% and black body temperature of 106°F. As the exposure time progressed, samples of the system were removed and examined by IR, fluorescence, and UV. The first samples were removed at 154.8 hours and the last samples after 1316.7 hours. In close examination of the infrared spectra these samples, no noticeable change could be detected in the spectra. Likewise no changes in the UV or fluorescence spectra of the materials were noted. Based on the data, model compounds do not behave as the polymer Nomex on exposure to UV light. The model amides are photochemically stable under the exposure conditions.

Nomex films, however, exposed to the above UV conditions showed extensive degradation after 40 hours, with yellowing and extreme fragileness. Infrared spectra were obtained from these samples and compared to unexposed samples, as well as, differential infrared spectra. There was a shoulder forming at 1720 cm^{-1} and filling in of the troughs in the spectra of the exposed samples. A 1370 cm^{-1} peak was also found in the spectra. These agree with the data Carlson found by attenuated total reflectance infrared studies.

Recently, Roylance and Devriees found that Kevlar contains a radical concentration in the yarn as high as 10^{18} spin/cc. This finding has been confirmed in experiments here. Nomex and Kevlar yarn both contain radicals with Kevlar having the largest number.

Three Nomex and Kevlar samples were prepared so that the same amount of yarn was exposed to irradiation by carbon arc. The samples are as follows:

		wt.(g)	exposure time
1)	Nomex	a) 0.1029	0
		b) 0.1048	39
		c) 0.1037	90.1
2)	Kevlar	a) 0.2026	0
		b) 0.0986	39.1
		c) 0.2018	90.1
		d) 0.2042	131.1

The standards were not exposed but their electron spin resonance (ESR) spectra were recorded under the same conditions as the exposed samples. The ESR's for the samples were double integrated and the areas compared to the standards. The following date was obtained:

		Area	Relative Amounts	Exposure Time
1)	Nomex	a) 12836	1	0
		b) 512100	70	39
		c) 1268880	99	90.1
2)	Kevlar	a) 6.45×10^6	1	0
		b) 1.408×10^6	2.2	39.1
		c) 1.018×10^6	1.58	131.2

The data shows a hundred-fold increase in the number of radicals in the 90 hour sample, while the Kevlar concentration remains the same over the duration of the exposure. These differences indicate that Kevlar contains long lived radicals buried in the polymer. Kevlar may contain an equilibrium concentration of radicals since there was no change in the radical concentration. The Nomex, however, generates radicals and these radicals may be the intermediates which cause Nomex's photoinstability. The radicals may be considered short lived relative to Kevlar, since meta substituted systems cannot stabilize the radicals to the same extent as Kevlar. Generation of the radicals in Nomex at least should lead to a drop in the $\bar{M}w$. The radicals may be quenched before recombination can occur and this would cause a drastic change in the $\bar{M}w$, as noted by Carlson.

Conclusion

1) The model compounds did not behave as the polymer Nomex in UV exposure experiments.

2) Since the models are dimer units and are stable, one must consider that some unit larger than the repeat unit of Nomex is responsible for degradation. An impurity in the polymer is a second attractive possibility.

3) Large members of stable free radicals are present in Kevlar. Nomex also contains stable radicals and the concentration increases on exposure of Nomex to UV light.